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Chemistry addressing sustainable development and other challenges of the 2020s

Abstract Book

“Safety First Culture” in Australian Laboratories

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Research laboratories conduct work at the vanguard of innovation and technology. This often entails working with hazardous materials and equipment, and untested reactions. Hazards can include biological, chemical, physical, radioactive, handling research animals and repetitive tasks. There are relevant Standards, Codes of Practice, Guidance Notes and legislative documents to assist staff and students to achieve laboratory safety compliance. To achieve a culture of safety that goes beyond compliance requires an integrated approach of responsibility and accountability, routine risk assessment, step-by-step procedures and competency. In an ideal laboratory safety culture, everyone who works in a laboratory, from inexperienced students to senior investigators, understands that they are operating in an environment that requires precautions. They are aware of the hazards posed by the materials and equipment they are working with in the lab, and they are able to take appropriate and timely measures to protect themselves and their co-workers, especially when unexpected events occur.

The presentation will draw on the experiences of Australia’s largest and most diverse science agency, the CSIRO, to demonstrate how a culture and mindset of laboratory safety has been developed and embedded to achieve safe people, safe work and safe science. Highlights will cover the processes, systems and tools to engage leaders, staff and students in safety critical behaviours, knowledge and skills.

3D LIGHT CONTROLLED MOVEMENT OF MICRODROPLETS

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The controlled transport of chemical species in fluidic environments has been key to the evolution of life on earth. Nature achieves this through the movement of complex vesicles such as motile cells and bacteria, typically in response to an external stimulus. Understanding and emulating such structures and processes in the fluid environment is one of the grand challenges confronting nanoscience today and has been the subject of intense research activity over the last ten years.

The simplest approach to the development of artificial motile vesicles has been the use of liquid droplets whose movement is generally the result of changes in surface tension or Marangoni effects. This has resulted in the fabrication of either relatively simple droplets whose motion is controlled by the external environment or more complex self-propelled droplets containing a chemical "fuel" to power the droplet movement.

We have developed a simple droplet system whose movement and direction can be controlled solely by light through changes in surface or interfacial tension. The droplets consist of a solvent containing a photoisomerizable (spiropyran) molecule and associated surfactant, and can move at extraordinary speeds of up to 10 mm s^{-1} towards or away from the direction of irradiation depending on the light (ultraviolet or visible) and the type of photoactive material used. In this paper, we will discuss the development of light-induced droplet movement (photochemopropulsion), how the droplet chemistry can be adjusted to achieve 3D movement in pure water, and doing chemistry through the interaction of two or more droplets.

A “universal” mechanism on the hydrogen induced corrosion of steels

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Abstract:

The presence of absorbed hydrogen (H) within steels tends to increase their corrosion. Atomic H is a strong reducing agent and this phenomenon has been attributed to the H-induced reduction of the protective passive film formed upon the metal surface. Recently, it was discovered using atomic emission spectroelectrochemistry that H promotes metal dissolution even in non-passivating solutions wherein, a passive film may not even be present upon the metal surface. This indicates that the mechanism of H-induced corrosion of steels is “intrinsic” as absorbed H could weaken metallic bonding within the steel and not necessarily “extrinsic”, involving destabilisation of the passive film. In electrochemical tests, H is usually introduced into steels by cathodic charging, where the metal is polarised for long durations at cathodic potentials ($< -1.2\ V_{SCE}$). The absorption of H into the steel occurs in parallel with H adsorption and H recombination during cathodic charging, however at relatively slower rates. Herein, we have studied the impact of absorbed H on the electrochemical properties of a martensitic SS (AISI 410). This particular SS is known to be prone to H-induced corrosion and sulphide stress cracking in “sour” environments. We used different electrochemical techniques and also inductively coupled plasma-atomic emission spectroscopy (ICP-OES) to evaluate the effect of H on the corrosion characteristics of this SS. The results have been used to determine the efficiencies of H absorption into the SS during cathodic charging and also to conceive a “universal” mechanism on the H-induced corrosion of steels.

A chemist's approach to single molecule super resolution microscopy

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Single molecule super resolution (SR) microscopy allows visualization of nanoscale distributions and architectures and has, since its invention a decade ago, already demonstrated huge potential for applications in both nanomaterials, and cellular and molecular biology. Its highly interdisciplinary nature requires collaboration between various scientific fields with the chemical sciences serving as the cornerstone of successful SR research. This is particularly evident as it relates to chemical fixation of biological specimens. Using correlative Synchrotron infrared spectroscopy/SR, we have shown how changes in reagent, temperature, concentration, timing and ordering of cell fixation steps can drastically alter the nanoscale landscape of cellular components, impacting the ability to draw biologically relevant conclusions from SR images. By understanding the chemical reactions and kinetics that modulate fixation, protocols can be optimized for the biological question of interest, yielding, for example, different protocols for investigating the effects of pathogenic proteins on cellular cytoskeleton ultrastructure compared to protocols for probing damage-induced morphological changes to chromatin. Development of new fluorescence labelling approaches is another chemistry-dominated area of SR research; although confocal microscopy protocols have proven useful, the enhanced single fluorophore sensitivity of SR has opened the door for new ideas. In our research examining DNA damage response pathways, we use cellular machinery to incorporate nucleotides or amino acids contained terminal alkyne groups into targets of interest that are then fluorescently labelled via 'click' chemistry. This allows visualization of single replication forks and transcription sites and their associated proteins, as well as quantification of the rates of these cellular processes.

A General and Efficient Synthesis of 5,6-Dihydrodibenzo[*b,h*][1,6]naphthyridines

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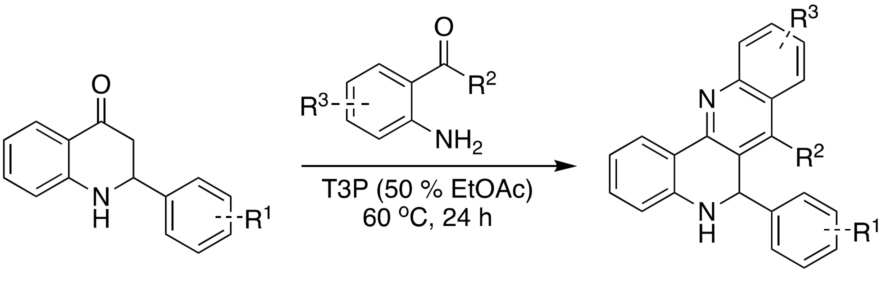
Dependensin is a dimeric flavonoid isolated from the root bark of a Tanzanian medicinal plant, *Uvaria dependens*, and has been shown to possess potent antimalarial activity. Extensive research has been conducted on new anti-malarial compounds, focusing on the flavonoid systems most closely related to dependensin. However, analogous systems in which the heterocyclic oxygen atoms of dependensin are replaced with nitrogen atoms, generating the [1,6]naphthyridine moiety, have been relatively unexplored. [1,6]Naphthyridine has been shown to possess a range of antiviral and anticancer properties. Furthermore, the [1,6]naphthyridine structure is highly fluorescent. Thus, compounds based on this nucleus have the potential to be used as fluorescent probes for medical imaging or as tags for diagnostic applications.

We report an efficient two-step procedure for the synthesis of dihydrodibenzonaphthyridines from benzaldehydes and 2-aminoacetophenones, proceeding through dihydroquinolone intermediates. The synthetic protocol uses the versatile and robust Friedlaender coupling methodology, and allows for the synthesis of a range of [1,6]-naphthyridines. This reaction does not require expensive catalysts and allows for the efficient isolation of pure products in good yields. Additionally, it allows the synthesis of more diverse analogues, closely related to the dependensin natural product.



A new perspective on nanoscale dynamics with ultrasensitive optical microscopy

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ABSTRACT TEXT

Mesoscopic structure and dynamics are central to a variety of key processes in nature, such as crystallisation, force generation or metastasis. An impressive number of techniques have been developed over the past decades aimed at understanding the underlying mechanisms, leading to both remarkable levels of knowledge with respect to both molecular and in some cases atomic structure as well as the overall kinetics of (dis)assembly of the relevant macromolecular complexes and structures. A distinct challenge, however, remains with respect to our ability to directly visualise and thereby quantify these interactions and dynamics at the fundamental, single molecule level. I will show how ultrasensitive optical microscopy based on light scattering alone, in the form of interferometric scattering microscopy (iSCAT), can be used to study mesoscopic dynamics with single molecule sensitivity, specificity and resolution. I will illustrate these capabilities with recent studies of phase separation, interfacial dynamics and biological filaments. In fact, recent results demonstrate that iSCAT is sufficiently sensitive to operate as a single molecule mass spectrometer in solution, which could be transformative for our ability to study protein-protein and protein-substrate interactions.

A novel of anti-adhesion polypropylene mesh in abdominal wall repair: based on dopamine-inspired surface functionalization

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ABSTRACT: Polypropylene (PP) as one of the most common prosthetic materials has been widely used in intra-peritoneal repair. However, its adhesion with viscera severely had limited its application. Therefore it is critical to improve the PP surface with anti-adhesion property. In this work, based on dopamine-inspired chemistry, virgin PP (V-PP) mesh was first pre-treated with O_2 plasma, then it was facilely and sequentially dipped in dopamine aqueous solution and then graft chitosan (CS) on it, finally the anti-adhesion meshes was obtained. The formation procedure of a PDA/CS ad-layer was characterized by water contact angle measurements, ATR-FTIR, SEM, and XPS. Then the NIH/3T3 cells were cultured on meshes to evaluate the availability of anti-adhesion and biocompatibility in vitro. Finally the efficacy of the PDA/CS-coating as barrier for reducing postsurgical adhesions was evaluated using a rat abdominal wall injury model. The results show that PDA/CS ad-layer could be coated on PP surface efficiently. Compared with V-PP group, NIH/3T3 cells exhibited higher viability on modified groups by evaluated with CCK-8 method. In addition, NIH/3T3 cells grow into round-shapes on O-PP/PDA/CS surface. This indicates that the modification strategy can facilely lead to excellent properties of anti-adhesion. In vivo tests also indicated that meshes after treatment were effective in reducing adhesion formation.

A step closer to 3D-Microbatteries for sensors: integrating polymer electrolytes

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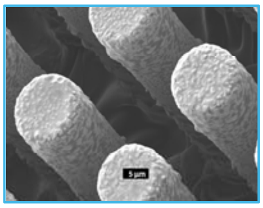
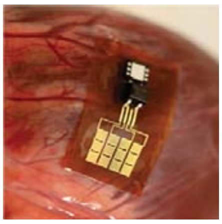
Today's sensor technology is undergoing a phase of miniaturisation to suit the requirements of many applications. These include, amongst others, medical devices and environmental monitoring. In many instances it is desirable for miniaturised sensors to operate wirelessly and autonomously, requiring a mountable and rechargeable power source of very small dimensions.

Current battery technology is not able to meet the demands of sophisticated miniaturised sensor devices. This project aims to develop a novel 3D-structured microbattery to power such miniaturised sensor devices. Here we present our approach to assemble a 3D-structured device with a particular focus on the incorporation of an ion conducting polymer film which functions as the electrolyte as well as a separator between electrodes. Notably, the polymer film is a ternary composite of polymer matrix, an ionic plasticiser, and a lithium salt. The effectiveness of the polymer to perform these functions was determined from electrochemical data.

3DMB Vision



Realisation



Application

http://www.the-scientist.com

A Stretchable and Flexible Glove Biosensor for Screening Chemical Threats

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Wearable chemical sensors are uniquely placed to fill the technology gap for real-time chemical analytics at the point-of-need. The seamless integration of chemical sensors within wearable platforms takes the power of laboratory-based chemical analysis directly to the user's fingertips. With this in mind, a flexible glove-based electrochemical biosensor with highly stretchable printed electrode system has been developed as a wearable screening tool for defence and food security applications. This disposable-mechanically robust "lab-on-a-glove" integrates a stretchable printable enzyme-based biosensing system and active surface for swipe sampling on different fingers, and is coupled with a compact electronic interface for electrochemical detection and real-time wireless data transmission to a smartphone device. An organophosphorus hydrolase-based biosensor system on the index finger enables rapid on-site detection of organophosphate (OP) nerve-agent compounds on suspicious surfaces and agricultural products. The new wireless glove-based biosensor system offers considerable promise for field screening of OP nerve-agents and pesticides in defence and food-safety applications.

Accelerated Protein Synthesis *via* One-Pot Ligation-Deselenization Chemistry

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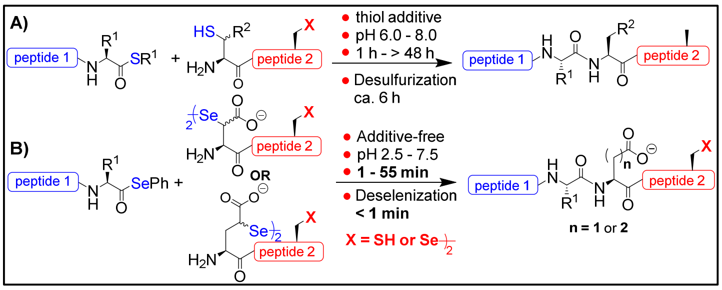
Native Chemical Ligation (NCL) is a powerful and widely applied method for the total chemical synthesis of homogeneous peptide and protein targets.[1] This method, which initially required a cysteine at the ligation junction, has been extended by the use of post-ligation desulfurization protocols[2] to enable the incorporation of non-proteinogenic amino acid building blocks bearing suitably positioned thiol auxiliaries. This one-pot ligation–desulfurization manifold has been successfully applied at a plethora of amino acid junctions.[3]

Despite such developments, NCL retains several limitations including the requirement for various additives to promote the reaction and a slow rate of ligation at sterically hindered C-terminal residues within the acyl donor peptide fragment. The recent discovery of selenium-mediated ligation chemistry, between peptides bearing an N-terminal selenocystine residue and peptides containing a C-terminal phenyl-selenoester, has been demonstrated to facilitate additive-free ligation reactions at unprecedented rates (1-5 min). The selenocystine-selenoester ligation can also be coupled with an in situ deselenization step to afford native peptide and protein targets in one-pot.[4] The scope of this rapid, chemoselective ligation-deselenization method is now being expanded to include the use of synthetic selenol-derived amino acids as selenocystine surrogates.

Remarkably, the use of β-selenoaspartate or γ-selenoglutamate as a selenocystine surrogate dramatically accelerates the rate of the radical-based chemoselective deselenization reaction. This has enabled the preparation of several polypeptides and proteins on unprecedented timescales.[5] The synthesis and application of β-selenoaspartate and γ-selenoglutamate will be described in this presentation.



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ACTIVATION OF CYTOKINE RECEPTORS: TURNING ON MICROMACHINES

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Atomistic molecular dynamics simulations have been used to investigate the conformational changes within the extracellular domain (ECD) of the growth hormone receptor (GHR)[1], the prolactin receptor (PRLR), erythropoietin receptor (EPOR)[2] and the epidermal growth factor receptor (EGFR)[3] associated with the binding or removal of ligand shedding new light on the mechanism of activation of these receptors at an atomic level. In all cases, the removal of the cytokine from the ligand-bound homodimeric receptor complexes results in a rotation of the two subunits relative to each other of between 30° and 45°. The magnitude and direction of the motion observed in the simulations of GHR and EPOR are in close agreement with experiment. The similarity of the motions in all these cases and in multiple simulations suggests that the relative rotation of the ECDs represents a general mechanism of activation of cytokine receptors.

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ADVANCES IN MULTI-COLOURED AND POTENTIAL-RESOLVED ELECTROGENERATED CHEMILUMINESCENCE

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Electrogenerated chemiluminescence (ECL) is the emission of light resulting from reactions between electrochemically oxidised and/or reduced species. This phenomenon has been exploited as a highly sensitive mode of detection (particularly in clinical immunodiagnostics) for many years. However, current commercial ECL systems are almost exclusively based on only one luminophore (tris(2,2′-bipyridine)-ruthenium(II)), which has been derivatised to create a variety of useful ECL 'labels'. The creation of new ECL luminophores and detection strategies, spurred by recent advances in the synthesis of iridium and other metal complexes, promises superior limits of detection and the enticing prospect of simultaneously detecting multiple spectrally distinct and/or 'potentially resolved' ECL luminophores.

The development of these systems requires the judicious design of metal complexes with specific electrochemical and spectroscopic properties, and a new understanding of not only the light producing pathways of each metal complex, but also the electron-transfer and energy-transfer pathways of mixed systems. This presentation will shows our conceptual pathways through several barriers that have restricted the application of highly promising iridium(III) luminophores as ECL reagents and labels, for conventional, multi-coloured and/or potential-resolved detection systems.

Aliphatic Aldehydes as Photolytic Sources of H_2 in the Atmosphere

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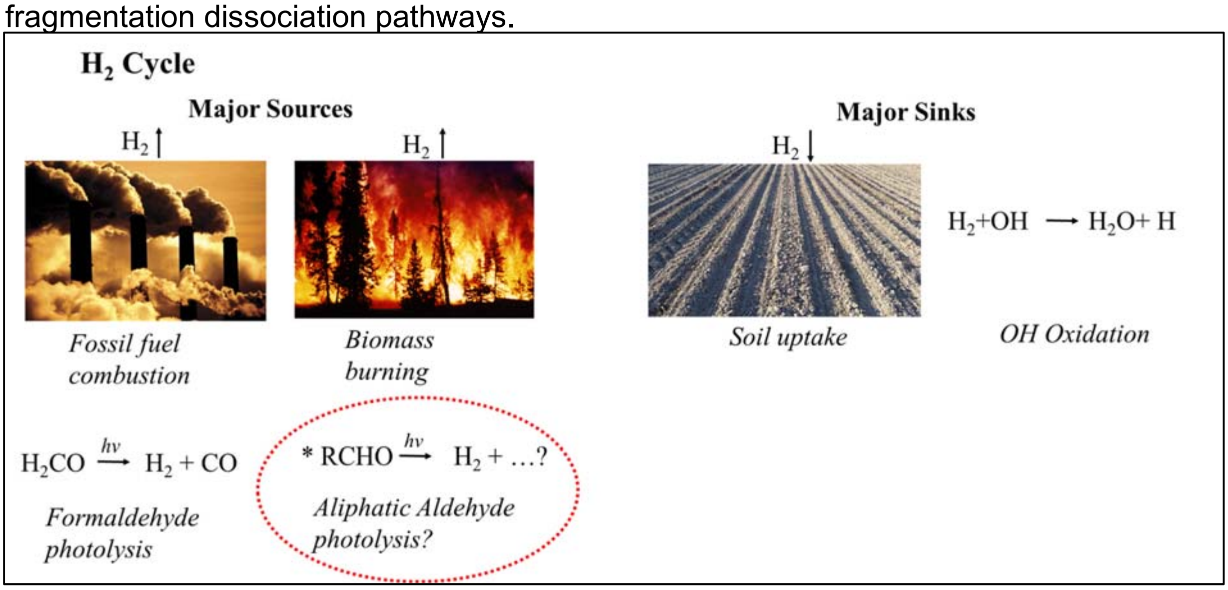
Molecular hydrogen is regarded as a potential replacement for hydrocarbons as a clean and renewable energy source providing motivation for efficient, large-scale production of H_2. This will likely lead to H_2 leakage into the atmosphere which is important as H_2 is an indirect greenhouse gas and impacts tropospheric concentration of OH and O_3.[1] A full accounting of the atmospheric H_2 budget is therefore of fundamental interest in the future H_2 economy. Currently, the major known sources of H_2 in the atmosphere are formaldehyde (H_2CO) photodissociation, fossil fuel and biomass combustion, and biogenic emission.[2] However, the present knowledge of H_2 sources and sinks is qualitative, and it has been suggested that additional H_2 production arises from photolysis of larger aldehydes which is unaccounted for.

We have recently made the first experimental observation of a photodissociaton channel of acetaldehyde leading to formation of ketene (CH_2CO) and hydrogen (H_2). This was accomplished using two complimentary experimental techniques. The H_2 photofragment was investigated utilizing a velocity-map imaging (VMI) apparatus, while the quantum yield of ketene production was characterized following acetaldehyde photolysis in a FTIR gas cell. With the velocity-map imaging results, we provide a detailed investigation of the photodissociation dynamics of this product channel while the FTIR results allow us to determine the quantum yield of this process under atmospheric conditions. In addition, using these methods, we have evidence for photolytic production of H_2 from two other aldehydes: propanal and isobutanal which have low barriers to H_2 production via triple fragmentation dissociation pathways.



All-Chemically Bonded Crosslinked Polymer Nanocomposites with High Energy Density

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ABSTRACT TEXT

Rapid evolution of energy storage devices facilitate the development of high-energy-density materials with excellent heat resistance and easy processing. The investigation for such materials has triggered the development of high-temperature, high energy storage and high charge-discharge efficiency polymer nanocomposites. However, the increase of fillers usually suffers from sharp reduction of breakdown strength, which is detrimental to substantial increase of energy storage capability.[1-4] Herein, this work reports the advances of utilizing a benzocyclobutene (BCB) surface functionalized $BaTiO_3$ nanoparticle (BT-BCB) and a polymer matrix of poly(arylene ether sulfone)s containing side propenyl groups (DPAES), creating a new thought to prepare an all-chemically bonded crosslinked polymer nanocomposite through solution process. The elaborate BT-BCB was prepared by using chemical graft and heck coupled reaction and used as crosslinking sites of nanocomposites, which can form a strong covalent bond with the dienophile of DPAES through Diels-Alder reaction (shown in Fig.1). This all-chemically bonded crosslinked nanocomposites with high dielectric constant can withstand high electric field and significantly surpress dielectric loss, showing strong potential to enhance the breakdown strength and electrical energy storage capability of the composites. Under 1000 Hz, all-chemically bonded crosslinked nanocomposite with 10 vol % BT-BCB exhibits an dielectric loss of 0.002 that is almost 87.5% lower than that of BT@DPAES nanocomposites (0.016) (shown in Fig.2). More importantly, this nanocomposites exhibits enhenced breakdown strength when compared with the BT@DPAES composites. It is possible that the weaken of interface between nanoparticles and polymer matrix makes the migration of charge carriers surpressed.

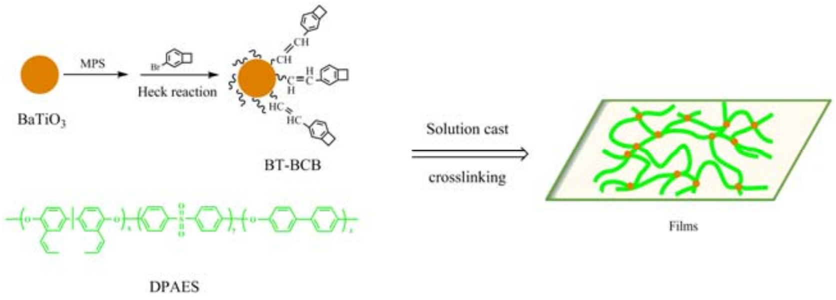

Fig. 1 Schematic illustration for preparation process of BT-BCB crosslinking sites and all-chemically bonded crosslinked nanocomposites.

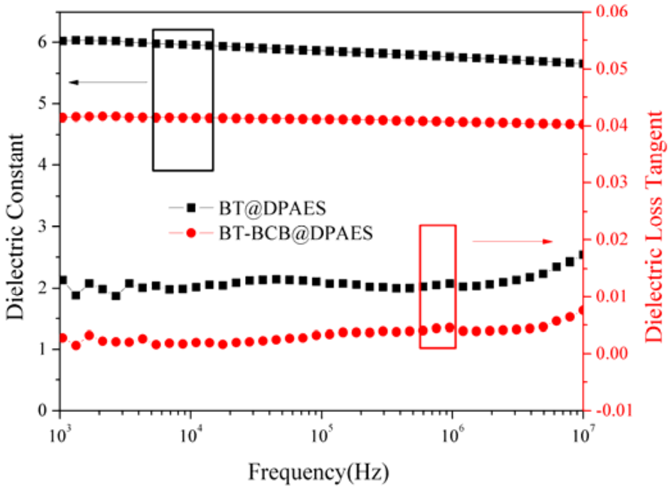

Fig. 2 Frequency dependence of dielectric constant and loss tangent of BT@DPAES, BT-BCB@DPAES (10 vol% nanofillers).

Keywords: all-chemically bonded, crosslinking, nanocomposite, dielectric properties, energy density

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Amyloid Fibril Architecture: From Atomistic to Micron Scale

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Amyloid fibrils are implicated in over 20 degenerative diseases. A detailed understanding of the molecular mechanisms of fibril self-assembly and amyloid nanostructure is essential to enable the rational design of therapies to prevent or reverse amyloid fibril formation. Furthermore, due to their unique structural and physical properties amyloid fibrils are finding important applications in biomaterials and nanotechnologies.

Short amyloidogenic peptides identified from disease related proteins such as lysozyme, transthyretin and tau (associated with forms of hereditary amyloidosis and Alzheimer's disease respectively) make ideal reductionist models to study amyloid self-assembly. Using a combination of nanoscale analytical and molecular modelling techniques, we have identified amyloidogenic peptides from globular proteins and characterised their self-assembly and nanoscale morphology at length scales from the atomistic to the micron. Such studies have allowed us to, for example, explain the origin of a rare right-handed twisted chirality in fibrils formed from hexapeptides identified in lysozyme (1), define a mechanism of assembly into previously unobserved giant amyloid ribbons in a peptide from Tau(2), and develop novel biomaterials from transthyretin based peptides(3).

Studies such as this will help us to develop a better understanding of structure-function relationships in disease related amyloids and aid the *de novo* design of amyloid based materials for biomaterial applications.

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An aptamer-targeted hyperbranched polymer for detection of triple-negative breast cancer

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Enhancing clinician's ability to prescribe therapeutic regimes and improve patient outcomes relies on improvements to early detection and diagnosis of cancers. Molecular imaging probes that are targeted to tumour cells are at the forefront of new approaches to image cancers both in vitro and in vivo. Within our research group we have focused on developing hyperbranched polymers (HBPs) synthesised by RAFT polymerisation which incorporate both targeting and molecular imaging modalities within a single construct.

The current work focuses on the production of HBPs targeted to the particularly aggressive triple-negative breast cancer. A facile polymeric synthesis approach allowed incorporation of multiple molecular imaging modalities as well as attachment of targeting aptamers to polymer chain ends utilizing copper-free azide-alkyne 1,3-dipolar cylcoaddition. The HPB is primarily composed of PEG-based monomers to enhance biocompatibility and increase circulation time. The construct incorporated a near-infrared fluorophore for optical imaging, as well as desferoxamine (A ^{89}Zr chelator) to enable clinically relevant positron emission tomography (PET) to follow long-term polymer behaviour *in vivo*. This multifaceted imaging HBP was then functionalized with an oligonucleotide aptamer which recognises the vascular endothelial growth factors (VEGF) 165 and 121, (Marusic 2013) that are over-expressed in triple-negative breast cancer.

The incorporation of long-lived PET isotope ^{89}Zr within such a targeted polymeric construct allows determination of long-term behaviour within the body. The *in vivo* behaviour and targeting efficacy of this aptamer-functionalized construct was demonstrated in a triple-negative breast cancer xenograft model.

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Analysis of Student Responses to Constructed Response Items in the National Assessment of Educational Achievement

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The present study aims at analyzing student responses to constructed response items in order to obtain detailed information on academic achievement and to draw suggestions for enhancing curriculum, teaching, and learning. The data is compiled of students' responses to constructed response items on the National Assessment of Educational Achievement(NAEA) in recent five years. Student responses were categorized according to type and characteristics were analyzed in relation to NAEA scores. Results based on the NAEA achievement level are presented and the nature of academic achievement is discussed. According to the analysis of the distribution curve of students' responses to the constructed response item of Matter, students have different misconceptions depending on their achievement level. Students in the Basic level tended to have misconceptions about the quantity of thermal energy, while students above Proficient level had misconceptions about the boiling point and thermal equilibrium. According to the analysis, students at the Basic level are not competent about the concepts of thermal energy while students above Proficient level are competent about thermal energy yet are confused by similar concepts. Therefore, according to the results, both understanding and misconception of students differed according to achievement levels so customized teaching and learning based on achievement levels should be developed. At the lesson planning stage, students' misconceptions should be considered and content should be organized to eliminate misconceptions. It was also suggested that troubleshooting based on students' misconceptions could be provided and accessed online to assist teachers in diagnosing students' misconceptions.

Antibiotic-Nitroxide Hybrids with Potential for Biofilm Control

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ABSTRACT TEXT

The adhesion of planktonic bacteria to surfaces, and their subsequent ability to aggregate into colonies called biofilms, is a critical issue plaguing healthcare systems around the world.[1-3] Biofilms are estimated to be involved in over 80% of all microbial infections in humans[4], including those associated with medical devices[5] and chronic wounds.[6] Bacterial biofilms exhibit extreme tolerance to conventional antimicrobial treatments, and consequently, it has become imperative to both investigate and develop new antibacterial strategies which utilise alternative mechanisms of action. We have recently demonstrated the ability of nitroxides to both inhibit biofilm formation and disperse existing biofilms.[7, 8] In this presentation, we will discuss the development, synthesis and evaluation of a new generation of fluoroquinolone based antibiotic, which couple the antibacterial activity of an antibiotic with the dispersal properties of a nitroxide free radical.

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ANTIFREEZE-PROTEIN MIMETIC POLYMERS FOR CELL STORAGE AND REGENERATIVE MEDICINE

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All modern biotechnology, basic biology and regenerative medicine relies on the ability to store cells (or tissues) for subsequent usage. For example, most biomaterials research is conducted on freeze/thawed immortalised cells. To enable the cells to be frozen large quantities of (toxic) organic solvents such as DMSO must be added, and subsequently removed. These solvents are not passive agents, causing phenotype changes, toxicity and can be a barrier in translational applications. Furthermore, many cell types cannot be cryopreserved efficiently using these methods.

We have developed the use of synthetic polymers which can mimic the function of antifreeze (glyco)proteins, AF(G)Ps, as new cell storage agents. AFGPs perform perhaps the most challenge recognition role in Nature – recognising the difference between ice and water. AFGPs are extremely potent at slowing ice crystal growth (recrystalisation) which is a major contribution to cell death upon thawing frozen cells. Here I will discuss recent progress we have made in the design, synthesis, ice growth inhibition and cryopreservation application of synthetic polymer mimics of AFGPs. In particular, the link between macromolecular structure and architecture on ice growth will be discussed and the use of these polymers to enhance the cryostorage of medically relevant cells will be discussed.

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ANTIMICROBIAL TERNARY COPOLYMERS THAT COMBAT PLANKTONIC AND BIOFILM BACTERIA

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ABSTRACT TEXT

According to the World Health Organization, the rise of multidrug-resistant bacteria is now considered a critical global healthcare issue. To combat this, synthetic polymer chemistry represents a promising approach for developing new and effective antimicrobial agents especially given the significant advancements in the field over the last few decades.

In here, we report the development of new amphiphilic random copolymers that exhibit good antimicrobial activity toward Gram-negative bacteria (planktonic and biofilm state) while demonstrating excellent hemocompatibility. Furthermore, minimal resistance development in bacteria was observed compared to conventional antibiotics. The excellent biological properties of these polymers are due to the combination of three key components in the polymer chain (ie cationic, hydrophobic, and low-fouling functional groups).

This study represents an innovative platform for combating the rise of antibiotic resistance.

Application of chemometrics to air quality data

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ABSTRACT

There are growing concerns that air pollutants have diverse adverse effects on humans. In addition to these effects, airborne particles scatter light, absorb solar and terrestrial radiation, affect atmospheric energy balance and influence the formation of clouds and precipitation (Teller and Levin, 2006). The primary parameters that determine the aforementioned effects are the sizes and compositional characteristics of the airborne pollutants. Given the need to mitigate these effects, ambient and indoor air are usually monitored for the presence of airborne contaminants and the large data sets obtained are subjected to different chemometrics methods to extract detailed information that would not otherwise be evident.

This talk will discuss the salient features of the results of our application of various chemometric techniques such as the multi-criteria decision making methods, PROMETHEE and GAIA, cluster analysis and receptor modelling techniques, including the two-way and three-way positive matrix factorisation to air quality data measured in different microenvironments and jurisdictions. It will also demonstrate how the chemometric analyses have facilitated the identification of the sources of the pollutants, contribution of each of these sources to different microenvironments and, in tandem with conditional probability function analysis, assisted the estimation of the most probable locations of the sources. Such detailed information has the potential to guide the number of air monitoring stations required in a region, aid the formulation of pollution mitigation strategies, and inspire the prioritisation of remedial actions that are based on scientific evidence.

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Application of Halogen Bonding to Catalysis and Supramolecular Chemistry

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Halogen bond, a noncovalent interaction involving a halogen atom as an acceptor of electron density, has emerged in recent years as an important element of molecular recognition and has numerous applications such as molecular self-assembly of functional materials and protein-drug interaction. Due to its bond strength and directionality, halogen bonding has great potential to become a complementary molecular tool to hydrogen bonding in rational catalyst design and crystal engineering. Using density functional calculations, we have shown the use of halogen-bond donors as noncovalent activators in Lewis acid catalysis. In this talk, we report our computational studies on two halogen bonding (XB) based catalysts, namely triaryl benzene and bis-bipyridinium with multiple **iodine-containing** groups, and their applications to Diels-Alder reaction, Claisen rearrangement, cope-type hydroamination and [3+2] cycloadditions. In recent years, halogen bonding has been fully exploited as a supramolecular synthon in the field of crystal engineering. Aromatic systems are potential halogen bond acceptors in supramolecular assemblies. However, the nature of interaction and geometrical features of halogen bonding involving π and aromatic systems are not well understood. Here, we will report our high-level ab intio study on 72 halogen-bonded complexes involving a range of π system. Our study reveals that the site of interaction in the aromatic systems is regiospecific.

APPLICATION OF RADIOCHEMICAL TECHNIQUES TO CHARACTERISE A RADIOACTIVE LEGACY SITE

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The Little Forest Legacy Site (LFLS), located near Sydney (Australia) presents unusual challenges for radiochemical analysis. In the 1960s this site was used for trench disposal of low-level radioactive wastes, which were mostly generated by the Australian Atomic Energy Commission (AAEC)[1]. These wastes arose from research into nuclear power generation and associated activities. While the disposals followed the prevailing international practices of the time, it is now recognised that these types of sites require careful monitoring and in some cases remediation. Many of the radioactive contaminants present at LFLS are rarely encountered in natural environments, other than at the trace levels associated with fallout from nuclear weapons tests. As a result of the types of wastes disposed at the LFLS (including fission products, transuranics, and activation products), analytical techniques for quantifying alpha-, beta- and gamma emitters, and in many cases complex radiochemical separation procedures, are required. More sensitive techniques such as Accelerator Mass Spectrometry are being applied to differentiate isotopes of various actinides, including those of plutonium and uranium[2]. A number of previous papers have discussed the scientific findings from the work, including the distribution of tritium[3] and the mechanism of plutonium mobilisation[4]. Considerable effort has been made to differentiate the radioisotope signal from the LFLS from other sources of radioactivity including global fallout from nuclear weapons tests[5]. This presentation will focus on the important underpinning role of radiochemical analysis, which has led to reliable data being obtained on the distribution and behaviour of radionuclides including ^{3}H, ^{60}Co, ^{90}Sr, ^{137}Cs, various uranium isotopes (^{233}U, ^{234}U, ^{235}U, ^{238}U) and transuranics (^{239}Pu, ^{240}Pu, ^{241}Am).

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APPLICATION OF SENSOMICS TO COMMERCIAL FLAVOUR ANALYSES

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ABSTRACT TEXT

Delivery of consistent odour is important for consumer acceptability of food. Many commercial companies use the "Sensomics" approach to identify and quantify key odorants in their products [1]. Sensomics combines bioactivity-guided detection of key odorants using gas chromatography-olfactometry (GC-O), accurate odorant quantification, aroma reconstitution and sensory omission experiments. There are over 100 peer-reviewed publications using this approach, identifying key odorants in over 200 food products. Food companies tend to use Sensomics differently to academic researchers, and its application to two food products, as well as some modifications to speed the analysis, are described here.

This paper used the GC-O step in the Sensomics approach to study changes in odorant compounds in a thermally processed product (roasted macadamia nut) and a stored/ matured product (fragrant rice). Results successfully identified the key changes in odorants between unroasted and roasted macadamia nuts and batch-to-batch variation in fragrant rice samples.

Two GC-O methodologies were compared; Aroma Extract Dilution Analysis (AEDA), as often employed in Sensomics publications, where odorant priority is assigned by calculation of Flavour Dilution (FD) factors; and Modified Frequency (MF), a more time-efficient methodology, where odorant priority is assigned by odour intensity and frequency of detection. Statistical comparison of the data from AEDA and MF showed no significant differences between assigned priorities of odorants identified. However, MF was able to identify more GC-O odour peaks in a shorter time.

In summary, Sensomics is a useful tool for commercial flavour researchers and, in examples given, the GC-O stage can be accelerated using MF.

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APPLICATION OF THE CRYSTALLINE SPONGE METHOD FOR NATURAL PRODUCT STUDIES

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ABSTRACT TEXT

The determination of the complete structure of natural products presents a major structural challenge since a majority are isolated in low quantities and many are only obtained as oily compounds, thereby precluding analysis via X-ray crystallography. The application of the crystalline sponge method to deduce the absolute structures for several marine natural products as well as the revised structure for a plant natural will be presented. Most of these structures were established on the microgram scale by the crystalline sponge method and the use of a porous coordination network (a crystalline sponge) capable of absorbing organic guests. In the sponge, the absorbed guests are ordered and are therefore crystallographically observable. The crystalline sponge method has now been used to successfully deduce the absolute structures of both synthetic and naturally derived compounds and is a revolution in complete structure determination. Its ability to establish the absolute configuration of highly complex bioactive natural products is extraordinary and is certain to pave the way for the re-analysis of many synthetic or natural compounds, especially in the field of drug discovery. Whilst limitations of this approach include the necessity for expertise in sponge methodology and crystallography and the fact that not all molecules will be absorbed by the sponge method, this complete structure elucidation package approach, where achievable, is remarkable.

Aqueous Labelling Method for [18F]Aluminium-Fluoride NOTA-Ubiquicidin(29-41), an Infection Imaging Probe.

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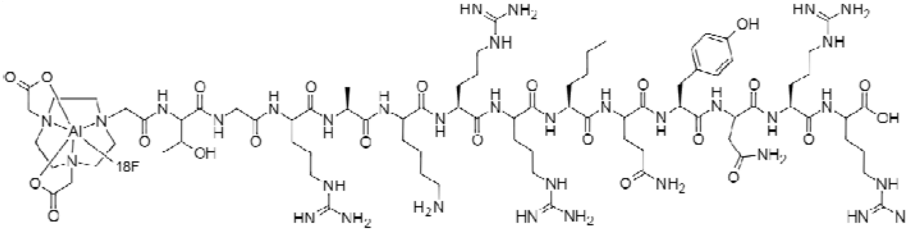
Due to the superior PET imaging properties of ^{18}F, the simple transition from generator-produced ^{68}Ga tracers to cyclotron-produced ^{18}F analogues is an attractive goal in radiopharmaceutical science. The recent efforts toward a suitable ^{18}F-compound to replace the widely successful prostate cancer probe ^{68}Ga-HBED-PSMA demonstrate this. The inherent difficulty is that though ^{68}Ga and ^{18}F-compounds (and the typical methods for preparing them) are vastly different, they are expected to exhibit a similar bio-distribution *in vivo*. A possible solution is to use ^{18}F in the form of [^{18}F]-AlF^{2+} ion and employ a chelate that can bind either ^{68}Ga^{3+} or [^{18}F]-AlF^{2+} ions, such as 1,4,7-triazacyclononane-N,N′,N″-triacetic acid (NOTA). Commercially available NOTA-Ubiquicidin, a precursor for the infection imaging probe [^{68}Ga]-Ubiquicidin(29-41), was chosen as a model compound to investigate this possibility.

The title product (**1**) was successfully prepared, affording a clean product in ~20 min without HPLC purification. Its stability in human plasma at 37 °C was assessed and compared against the ^{68}Ga-labelled analogue. Similar assays of labelled HBED-PSMA were also performed. Although **1** was stable in formulation, the product slowly degraded in plasma (RCP 50% at ~1 h). Under the same conditions, some degradation of the ^{68}Ga analogue was also observed, but this process was more gradual. Similarly, under identical conditions the clinical compound [^{68}Ga]-HBED-PSMA was quite stable in human plasma whereas its [^{18}F]AlF-labelled analogue degraded over time - however this degradation appeared to follow a route other than simple loss of [^{18}F]AlF^{2+} ion. Though degradation in plasma may be of some concern due to potential uptake of ^{18}F in bone, by a careful choice of chelate this strategy remains a promising route for the simple preparation of ^{18}F-analogues of existing ^{68}Ga products.



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Assemblies of glyco-engineered macromolecules: from nanobiotics to minimal artificial cells

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Many biological events proceed by specific carbohydrate – protein interactions that lead to receptor mediated endocytosis (RME) processes. Multivalent glycosylated macromolecules can be used as targeted drug delivery vehicles to specific cells and the sugars bring about internalisation via RME. From the molecular recognition perspective, construction of supramolecular glycomimics that can interact with biological entities through the language of the "glycocode" and thus develop a simple model of biological cells and vehicles for targeted drug delivery remains a central challenge.

The presentation will describe the synthesis of well-defined amphiphilic glycopolymers *via* post-polymerisation functionalisation with aminoethylglycosides of preformed well-defined block polymeric activated ester (poly(pentafluorophenyl acrylate)-*b*-poly(n-butyl acrylate)) prepared by RAFT polymerisation. The self-assembly of the produced glycopolymers in aqueous solution using different methods to form various morphologies ranging from nano- to micro- scale with sugar moieties presented on the external surface will be presented. Subsequently, the application of these sugar-decorated nano-scale particles as antibiotic delivery systems (glyconanobiotics) and micro-scale particles as simple protocell models displaying cell-like behaviour through a native receptor-ligand interaction will be discussed.

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Assembly of gold nanoparticle tetrahedra using DNA scaffolds

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Programmable assemblies of metal nanocrystals on DNA scaffolds have been extensively used to design plasmonic nanostructures. In particular, three-dimensional nano-assemblies can be produced by encoding tetrahedral symmetry into four thiolated DNA strands. The thiol groups allow attachment of four nanocrystals, one to each tip of the tetrahedron. This geometry can exhibit circular dichroism (CD) when using different materials or sphere sizes, therefore displaying great versatility and potential as a metamaterial. Nevertheless, despite these attractive properties, the tetrahedral assembly of gold nanocrystals has been little described. This comes from the difficulty of controlling the number of DNA strands attached to individual nanoparticles that is required to avoid any undesired geometries. Furthermore, the nanocrystals have not been fully proven to adopt a 3D tetrahedral arrangement in solution.

Here, we investigate multiple approaches to fabricate tetrahedral nanostructures. The common first step consists of hybridizing DNA strands on gold nanospheres and isolating particles with a single DNA tethered on their surface using electrophoresis. Because all four strands used in this step have complementary sequences, mixing these particles can produce dimers, trimers or tetramers with variable yields. By testing all possible combinations, we aim to find the optimal approach to fabricate tetramers. Using cryo-TEM we present the 3D morphology of these nanostructures in solution for the first time. This optimal method can subsequently be used to fabricate tetrahedra with four spheres of different sizes instead (range: 8-35 nm). This paves the way for the controllable fabrication of more complex 3D plasmonic structures in high yield.

Asymmetric Hydrogenation of Aromatic Bisheterocycles Using Chiral Cationic Ru(diamine) Catalysts

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Optically active heterocycles are important structural motifs of many biologically active compounds, natural products, and chiral ligands. Accordingly, many methods have been developed for the synthesis of such chiral compounds. Among them, asymmetric hydrogenation of readily available heteroaromatic compounds represents one of the most straightforward and efficient approaches. Over the past decade, a variety of heteroaromatic compounds have been hydrogenated with excellent reactivity and enantioselectivity [1]. However, asymmetric hydrogenation of heteroaromatics bearing more than one heterocycles, particularly adjacent bisheteroaromatic substrates, has been less exploited and remains a challenging task. On the basis of our previous work on the asymmetric hydrogenation of various N-heteroaromatics catalysed by Ru(diamine) complexes [2], herein, I will report our recent results on the ruthenium-catalysed asymmetric hydrogenation of some difficult N-heteroaromatic substrates bearing two pyridyl rings [3]. The related mechanism will also be discussed in this presentation.

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ATR-FTIR spectroscopy studies of polymer-based cards used for identification

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Polymer-based cards are widely utilised in society as identity cards, driver's licences, health and government services cards, credit cards, loyalty cards, etc. Many of these are required to prove a person's identity when accessing financial accounts or payments, or are issued identity documents such as passports. For this reason these types of cards can be a target for counterfeit production locally, nationally and internationally. Detection of counterfeit cards currently relies on visual examination by people with minimal or no training, with referral of the card to a forensic document examiner only when suspected of being counterfeit. This process is based on subjective assessment and could be improved by implementing a simple, rapid and robust method to determine if the card requires further examination. One approach is to use chemical characterisation in combination with chemometric analysis of the data. Chemometrics can ensure quantitative, objective measures of a dataset are obtained; thereby improving reliability, reproducibility and discrimination of the data, whilst simultaneously addressing issues concerning observer bias and other sources of human error in forensic examinations.

The studies presented here describe the characterisation of polymer-based identification documents using attenuated total reflectance-Fourier Transform infrared spectroscopy (ATR-FTIR). The subsequent classification of the cards through the use of chemometric techniques will be discussed as an additional avenue for the detection of counterfeit cards. Synchrotron infrared microscopy was employed to characterise the chemical composition of the polymer cards, the high spatial resolution and brightness of synchrotron infrared enabling a closer examination of the layer structure.

Benchmark Calculations of Ligand-stabilised C_2

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The ‘bare’ C_2 molecule has attracted significant interest recently, in addition to ligand-stabilised forms of C_2. Despite being a small molecule, a number of properties are not well known for ligand-stabilised small carbon clusters (in the zero oxidation state). Here we report results of a theoretical investigation of ligand-stabilised carbon chains, including N-heterocyclic carbine stabilised C_2 (a rare example of a *cis*-stabilised alkene) [1] and OC-CC-CO. For C_4O_2, the singlet-triplet gap is not well known (it is a ground state triplet). High-level coupled-cluster calculations up to CCSDTQ will be reported, which provide an accurate estimate of the singlet-triplet gap for OC-CC-CO. For the cis-stabilised NHC-C2-NHC system, high-level calculations are required to confirm the experimental observations.

BIOACTIVE NANO- AND MICROSTRUCTURES FROM SELF-ASSEMBLING AMPHIPHILIC GLYCOPOLYMERS

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Carbohydrates mediate many processes in biology, particularly those that involve contacts between surfaces (for example cell-cell and cell-virus particle contacts). Nature overcomes the intrinsic weakness of individual carbohydrate-protein (lectin) interactions by means of multivalency, of both the carbohydrate ligand and the lectin. Thus the preparation of multivalent, high-affinity carbohydrate-bearing macromolecules, including glycopolymers, is an attractive strategy for investigating and inhibiting such interactions, leading to applications in therapeutics, diagnostics, protein purification and other areas of biotechnology. We present our work on the development of biologically active, amphiphilic glycopolymers from simple monosaccharide-containing monomers. Depending on the exact molecular characteristics of the polymers and the self-assembly process employed, the polymers can be assembled into a variety of bioactive nano- and microstructures, including micelles, nanoparticles and polymersomes. The presentation will discuss two recent projects in our lab: 1. The production of self-assembled glyconanoparticles for the delivery of antibiotics ('glyconanobiotics') [1]; and 2. The development of glycosylated giant polymersomes as simple minimal cell mimics [2].

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Biocompatible Near IR Photosensitizers for Cancer Theranostics

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

The development of biocompatible nanosystems for cancer therapeutics and diagnostics (theranostics) is highly desirable for preventing over- or under-treatment during cancer treatment. Aza-boron-dipyrromethene (aza-BODIPY) dyes, in which the *meso*-carbon atom of the classic BODIPY molecule is replaced with a nitrogen atom, displaying superior photophysical properties for applications in near IR fluorescence imaging and photodynamic therapy. It has been well recognized that the combination of strong fluorescence for diagnostics and the efficient generation of singlet oxygen for photodynamic therapy in one sensitizer used to be in conflict, because efficient excited state ($S1 \rightarrow T1$) intersystem crossing normally quenches the fluorescence. We describe here a self-assembled conjugate containing 3,5-dithiophene-substituted aza-BODIPY bound to the surface of CdSe QDs encapsulated by biocompatible FA-DSPE-PEG2000, resulting in high FRET efficiency, which may be used as a multifunctional photosensitizer for the targeting of live cells and simultaneous fluorescence imaging and photodynamic therapy via excitation in the near IR region.

Biodegradable Polymers for Controlled Nitroxide Release

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Bacterial attachment and growth of bacterial biofilms affects almost all aspects of our lives from large industrial challenges, i.e. biofouling on ship hulls or in food packaging, to medicinal effects like wound or implant infections. A variety of materials have been developed that can prevent bacterial attachment to surfaces, however, a passivation of the functional surface can occur for example by bacterial overgrowth.

A strategy to fight pre-formed biofilms is to induce biofilm dispersal exploiting signalling mechanisms that are usually responsible for biofilm proliferation. Nitric oxide has been identified to play a key role in this signalling process.[1] In combination with standard antibiotics, bacterial biofilms could be completely dispersed and eradicated.[2] Our group was able to show that nitroxides can induce similar dispersal processes in biofilms while being a stable and solid alternative to gaseous nitric oxide.[3]

This presentation will report the development of biodegradable polymers that contain nitroxides for potential applications in drug delivery, implants, or wound dressings, The degradation of the prepared polymers and the release profiles of the nitroxide building blocks from the polymers in aqueous environments will also be discussed.

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Bio-inspired superhydrophobic and superhydrophilic surfaces

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Superhydrophobic and superhydrophilic surfaces have been extensively investigated due to their importance for industrial applications. It has been reported, however, that the superhydrophobic/superhydrophilic surfaces are very sensitive to heat, ultraviolet (UV) light, and electric potential, which interfere with their long-term durability. Biological species in nature have developed unique structures and functions very close to perfection to suit their specific living environments after millions of years of evolution and selection, which offer us excellent inspirations on developing artificial nanomaterials with extraordinary properties. In this study, we introduce a novel approach to achieve robust superhydrophobic/superhydrophilic surfaces by designing architecture-defined complex nanostructures by learning from natural species. Bio-inspired ZnO nanostructures with designed wetting behaviors have been successfully fabricated by mimicking the natural photonic structures found in the cycloid scales of Asian Arowana (Scleropages) and the compound eyes of horse-flies (Hybomitra micans). The unique surface properties of the bio-inspired nanostructures open a new way to design novel multifunctional nanomaterials.

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Biomass Derived Sugar Dehydration on Heterogeneous Metal Organic Framework Catalysts

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ABSTRACT

Mitigation of reliance on finite fossil fuel resources is driving research towards the development of alternative renewable chemical feedstocks. Biomass is a promising alternative; from which simple sugars, e.g., glucose, can be obtained cheaply and efficiently. 5-Hydroxymethylfurfural is considered to be one of the most promising platform molecules that can be converted into a wide array of end user chemicals. However, conversion of glucose into 5-hydroxymethylfurfural remains a challenge. In this study we investigate the potential use of metal organic frameworks for glucose dehydration into 5-hydroxymethylfurfural. In addition, novel modifications and synthesis methods have been screened to develop metal organic frameworks, with desired properties to efficiently catalysts this reaction and environmental friendly. The advantage of metal organic frameworks is the ease of chemical modification with different types of metals and organic linkers. This provides an opportunity to introduce both Lewis and Brønsted acidity, as well as control over the acid strength and concentration on the catalyst surface. Our recent results on controlled modification of metal organic frameworks will be presented. The detailed structural characterization of metal organic frameworks using powder XRD, TGA, nitrogen adsorption and IR spectroscopy, along with their catalytic activity will be discussed.

Keywords: 5-Hydroxymethylfurfural, glucose dehydration, MOF, acid catalyst

BIONIC ARTIFICIAL MUSCLES

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ABSTRACT TEXT

Muscles are a nature’s motor. They are intriguing, chemically driven mechanical systems comprising an intricate hierarchical molecular structure that facilitates fuel delivery and waste removal; fast and powerful contractions; long lifetimes with self-healing; and in-built sensing for feedback control. Our attempts to replicate the performance of natural skeletal muscle has involved studies into the fundamental mechanisms of volume and / or shape change in polymer-based fibres and films in response to a range of input stimuli: electrical, chemical, photonic, thermal and combinations of these. Our artificial muscle materials do not yet match the structural intricacy of natural muscle, yet they do exploit amplification mechanisms seen in nature, such as when the materials are reinforced with helically oriented fibres, nano-filaments or oriented molecular chains. Even with a simplified structure, thermally-driven artificial muscles made from twisted and coiled polymer fibres can generate power-to-weight ratios that far exceed natural muscle. Of current interest is to enhance the energy conversion efficiency and to develop isothermal, room temperature operated muscles. New processing technologies like textiles processing and 3D printing are valuable tools in the production of devices exploiting artificial muscles.

Biosynthesis of Steroidal Saponins in *Dioscorea sp.*

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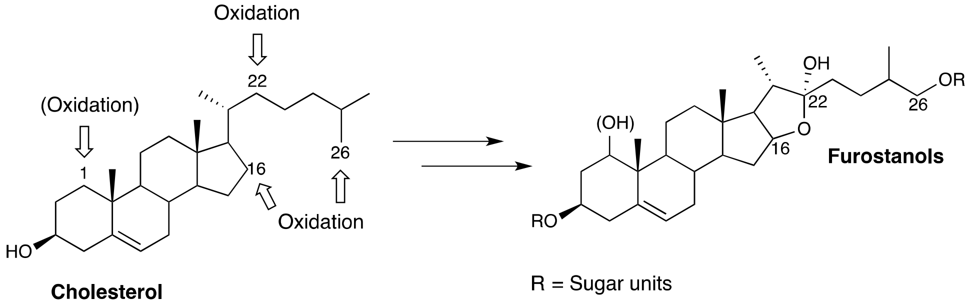
Steroidal saponins are common constituents in a variety of commercially important herbal medicines and are widely believed to be responsible for their therapeutic effects. These saponins generally consist of a polyhydroxylated cholesterol nucleus bearing a number of sugar moieties at varying positions: the positions of hydroxylation and the pattern, nature and degree of glycosylation combine to generate enormous structural diversity in this family. This diversity is mirrored in their bioactivities which include: cytotoxicity; anti-inflammatory, antitumor, antifungal, and immunoregulatory activity; hypoglycemic and cardiovascular properties. However, little is known of their biosynthesis and only the most simplified scheme can be proposed (Scheme 1).

We set out to explore saponin biogenesis, and in particular the monooxygenases required for cholesterol hydroxylation. The Australian native *Diocorea transversa* was chosen as a model plant as we had shown it to have a simple saponin profile, producing only protoneogracillin and its 1β-hydroxy derivative.

A transcriptome was generated from *D. transversa* yam, where the saponins were found and compared to one generated from leaves of the same plant. Cytochrome P450 monooxygenases were selected on the basis of level of expression and the known preference for steroidal substrates in some P450 families. The genes encoding these enzymes were synthesised and expressed in *E. coli* and the resultant proteins characterised. In addition, the cytochrome P450 reductase from *D. transversa* was cloned and expressed. The activity of these enzymes toward cholesterol and the chemical synthesis of a number of hydroxycholesterol derivatives will be discussed.



Scheme 1. Simplified Biosynthetic route to steroidal saponins.

BORONIC ACID CATALYSIS: A PLATFORM FOR DIRECT TRANSFORMATIONS OF HYDROXYL GROUPS IN ORGANIC SYNTHESIS

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Although boronic acids are recognized primarily for their utility in cross-coupling chemistry, other applications are emerging, including their use as reaction catalysts in a concept coined “Boronic Acid Catalysis” (BAC). To date, few methods are available for the organocatalytic activation of hydroxyl functional groups under mild conditions leading to their direct transformation into useful products. The ability of boronic acids to form reversible covalent bonds with hydroxyl groups can be exploited in the selective activation of allylic and benzylic alcohols to form carbocation intermediates that can be trapped with suitable nucleophiles. Classical Friedel-Crafts chemistry for alkylation of arenes, which employs strong Lewis acids to activate toxic alkyl halides, is not ideal from the standpoint of green chemistry. To this end, we identified ferroceniumboronic acid hexafluoroantimonate salt as an excellent catalyst in the direct alkylation of arenes with readily available benzylic alcohols. By featuring a new ion-redistribution mechanism, this catalytic method allows a wide range of primary and secondary benzylic alcohols to react at temperatures as low as 25 °C and afford pharmaceutically relevant diaryl- and triarylmethane products. In a promising evolution of this concept, we explored the application of dual catalysis combining BAC with amine catalysis for enantioselective enolate alkylation with allylic alcohols leading to acyclic quaternary carbon centers. More recently, our laboratory found that BAC is also applicable to the activation of N–OH units to accelerate the classical Beckmann rearrangement of oximes into amides.

Breaking Good: Open Research in Undergraduate and School Laboratories

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The Open Source Malaria (OSM) consortium has been pioneering open source drug discovery since 2011. The aim of the project is to find a small molecule that is effective for the treatment of malaria using open science principles.

All experiments are published on the Internet in electronic lab notebooks, all data are available for anyone to use and there will be no patents. One of the many advantages of this open approach is that barriers to participation are much lower than for traditional drug discovery projects.

The unique features of OSM have enabled us to develop a chemical education project, *Breaking Good*, whereby undergraduates and even high school students can take part in a real research project and synthesize new drug targets.

Over the past few years, undergraduates in the USA, NZ, UK and Australia have all worked on the synthesis of novel antimalarials and some of the molecules made show promising activity against *Plasmodium falciparum*. Additionally, a class at a local high school have contributed to OSM and recently synthesized the price-hiked toxoplasmosis medicine, Daraprim, in their high school laboratory.

Here we describe our efforts to increase inquiry-based learning and provision for exciting and informative practical science and our attempts to expand *Breaking Good* through platform development, training and crowd-funding to ensure that the project is sustainable.

BRINGING INDUSTRY INTO AN UNDERGRADUATE LABORATORY PROGRAM

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At Monash University the Transforming Laboratory Learning project is engaging industry to generate authentic laboratory lab classes to better prepare students for their careers, whether it is in Chemistry or another field.

The project engages industry in a variety of ways, from adding existing labs to comments on industrial best practice. Examples will be discussed that demonstrate the variety of ways in which industry connections can be woven into the undergraduate course on a day to day basis.

One such example is working with scientists at MARS Foods to convert a routine first year acid-base titration into an assessment of the acetic acid content in dressing from a real MARS recipe. In this case, MARS foods also supplied usage data and background for the laboratory. We also worked with Rationale (a Melbourne based personal care company) to turn a standard second year synthesis into a team based activity to select the best sunscreen ingredient.

Industry partners can also be a valuable source of additional learning materials (e.g. videos, industry websites, application notes) to engage students and get an up to date industry perspective. We worked with Dulux to make a short video to support a third year particle size characterisation laboratory. This video is linked into the students learning by being incorporated into the pre-laboratory questions.

By weaving workplace authentic experiences into the everyday laboratory curriculum, students can finish their degree with a better understanding of how scientists and laboratories work, thus empowering them to enter the modern workforce.

CAREER ASPIRATIONS OF UNDERGRADUATE CHEMISTRY STUDENTS AND GEOGRAPHIC DIFFERENCES

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University chemistry departments are concerned with major issues such as provision of quality education, enhancing and maintaining good learning outcomes of students, provision of excellent student experiences, and enhancing retention of students in their courses. One of the factors that affect learning outcomes has been identified as student aspirations. This study investigated career aspirations of undergraduate chemistry students from Australia, New Zealand and the UK. The study was in the form of a cross-sectional survey. The data were collected between 2014 and 2016. The results of the study showed that undergraduate chemistry students mainly choose to study chemistry because they like it and do enjoy it. Also, the majority of the students want to pursue a career that uses chemistry. However, the UK had a higher percentage of such students as compared to Australia and New Zealand. The results also showed differences in career preferences of students from different regions. This study forms part of a growing body of research on the influence of students' career aspirations on science education. The findings of this study may therefore inform good practices that would enhance the student experience and retention in university chemistry programmes.

Cataluminescence Gas Sensor for Volatile Organic Compounds

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In recent years, cataluminescence (CTL) generated on the surface of nanomaterials has also been investigated as a promising transduction principle for gas sensors. In contrast to sensing based on intrinsic analyte properties, CTL approach dramatically expands the range of detectable species by utilizing a series of responsive sensing nanomaterials, improves sensors performance, and is adaptable for miniaturization. Therefore, we focused on exploring the sensing materials, and established a series cataluminescence sensors for volatile organic compounds (VOCs), such as ethanol, ethyl ether, volatile chlorinated hydrocarbons, acetone, carbon tetrachloride, tert-butyl mercaptan, isobutanol etc. on different sensing materials, including controllable synthesized metal oxides, mixed metal oxides, and metal doped metal-organic framework. Besides, toxic gases such H_2S has also been recognized when adopted α-Fe_2O_3/C_3N_4 in our laboratory. Surely, the possible cataluminescence mechanism have been also investigated carefully. For example, theoretical calculation together with experimental investigation explained the reaction process and proved that $CH_3CO\cdot$ would be the possible luminophore during the cataluminescence of ethyl ether on borate glass. Last year, we developed a transient cataluminescence (TRCTL) concept for gas sensor, more than 10 VOCs was successfully recognized and the mechanism of the TRCTL phenomenon on the highly efficient sensing material was illustrated. In addition, we expect more catalysts with a variety of sensing characteristics to broaden the library of catalysts and to increase the ability of CTL sensor systems in identification of analytes.

Cation exchange capacity of agricultural soils using laser-induced breakdown spectroscopy (LIBS)

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Laser induced breakdown spectroscopy (LIBS) have been used for direct analysis and multi-elemental determination of different solids, including soil. The use of LIBS is beneficial for rapid soil measurements which are vital for routine assessments of agricultural lands. Soil pH, texture, and degree of humification are some of the soil properties that have been predicted recently from statistical models using LIBS. Another important soil property that has yet to be determined using LIBS data is soil cation exchange capacity (CEC). Soil CEC is routinely measured as this property influences structure stability, nutrient availability, pH, etc. of soils. LIBS can circumvent the shortcomings of conventional methods used in determining CEC which are time-consuming and labor intensive. Using the emission intensities of the following elements: Mg, Ca, Na, K, Al, C, H, O, N, P, Fe and Si, collected from various types of agricultural soils, a model for CEC could be established. The emission intensities were gathered using commercial LIBS equipped with laser operating at 1064 nm with 50 mJ pulse energy. This presentation will explore the development of a prediction model for the determination of CEC in agricultural soils. Sample preparation, optimization, several statistical modelling techniques using LIBS data, and comparisons with conventionally derived CEC will be discussed. Validity of the proposed CEC model will be compared to mid-IR spectroscopy measurements.

Charge Carriers Generated by Optically Pumping Excitons in P3HT Aggregates

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In a conjugated polymer solar cell, exciton mobility and dissociation are critical to device performance. Photogenerated excitons must migrate to a donor-acceptor interface where they can dissociate into their constituent electron and hole charge carriers. Due to the intrinsic disorder of the polymer domains, excitons may become trapped in local low-energy sites, inhibiting their contribution to device output.

Femtosecond pump-probe transient absorption spectroscopy has been used extensively to study exciton and charge transport in conjugated polymer systems, however analysis and interpretation of data can be challenging when several concurrent processes are involved. We employ a pump-push-probe technique to selectively "push" excitons in aggregates of poly(3-hexylthiophene) (P3HT) and isolate the signals of charge carrier generation by accessing a high-energy state.

Upon photoexcitation, P3HT exhibits induced absorption bands in the near-infrared (NIR) which can be assigned to singlet exciton and hole-polaron species. Upon targeting the exciton absorption with a NIR push, depletion of exciton and a corresponding increase in the polaron concentration are observed. With quantum calculations we assign the exciton absorption band to the S_1 to S_3 transition, and note the S_3 state displays some intramolecular charge-transfer character. We conclude that the NIR push acts to liberate trapped excitons and facilitate their dissociation through the charge-transfer nature of the S_3 excitonic state.

Charge transfer contributions to halogen bonding: implications for reactivity

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In the past decade, halogen bonding has experienced a renaissance due to its potential utility in applications such as crystal engineering, self-assembly, and catalysis. Although halogen bond (XB) interactions have been known for decades, only recently have systematic studies begun to probe the exact nature of this type of “non-covalent” interaction. Using X-ray absorption spectroscopy (XAS), we recently identified a surprisingly large degree of covalency (i.e. charge transfer) in certain charge-assisted halogen bonds. The measured degree of charge transfer is similar to that which is commonly associated with metal-ligand coordinate bonds and significantly greater than for hydrogen bonds. We explore the importance of this covalent contribution in a series of systems ranging from medicinally-relevant peptide/drug interactions to efficient XB-promoted electron transfer in dye-sensitized solar cells.

Chemical Reactivity in Ionic Liquids

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Ionic liquids are liquids composed entirely of ions. By careful selection of their cations and anions these can be prepared with melting points at or below room temperature. These ambient temperature ionic liquids have been the focus of much interest in recent years in both academia and industry. They are interest for a wide range of applications, such as solvents for synthesis and catalysis,[1] media for CO_2 capture,[2] electrolytes for energy applications,[3] and solvents for biomass dissolution.[4]

Early interest in ionic liquids focused on broadening the range of reaction that were demonstrated in ionic liquids. However, more recently several groups, including ours, have been interested in how ionic liquids can affect the reactivity of dissolved.

In this presentation we describe the effects of ionic liquids on a number of reactions, focusing on kinetic and mechanistic studies.

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Chemical Shifts In Sodiated Black Phosphorus Anode: A Density Functional Theory Study

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The increasing demand for rechargeable batteries and limitations in lithium resources has encouraged material scientists to search for alternative materials and systems for the next generation of batteries. Sodium-ion based batteries are one of the alternative choices and among them, the phosphorus-sodium systems with high theoretical capacity of 2596 $mAhg^{-1}$ seems to be one of the feasible choices. Although the structure and properties of pure Phosphorus and fully Sodiated phosphorus (Na3P) are well known, the structure of intermediate phases and their characteristics are still not well stablished. In this study we try to identify these phases and characterize their properties using sub-atomic computational schemes. Density functional theory (DFT) is employed in this study. Perturbation theory in DFT has been incorporated to measure the chemical shielding of different suggested phases of Na/P system. Three different energy functionals, having different computational demands and accuracies, have been used for the DFT calculations. The calculated chemical shielding tensors for phosphorus atoms in each of the phases are compared with the available chemical shifts from NMR experiments. The comparison results suggest that a mixture of phases exist along the sodiation and de-sodiation.

CHEMISTRY CHALLENGES IN THE ASSESSMENT AND CLEAN UP OF GREENFIELD DEVELOPMENT SITES

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ABSTRACT

Population growth in Australian cities means that agricultural land on the urban fringe is being developed for residential and commercial use. Contrary to expectations, such sites frequently contain contaminated soil and groundwater as a result of previous farm practices. The assessment and clean up such sites, prior to development, present different challenges compared with contaminated sites with a history of industrial use. Many of these challenges are related to the chemistry of the contaminants themselves, their uses and fate, and also that of the methods used to measure the extent and impact of contamination. Additionally, sampling methodologies and patterns suitable for large, broadacre sites can influence outcomes.

Across several such example sites in different climatic and soil conditions, including orchards and market gardens, the identification of contaminant sources, both from on-site activities and from off-site land uses, has required an understanding of the chemistry of products such as pesticides, fertilisers and fuels. Also, an understanding of elements of the contaminant chemistry has aided in risk assessments for contaminated soil and groundwater, particularly where contaminant mixtures are present, either as result of environmental degradation or simply because of the mode of chemical use. Field measurement techniques commonly used in contaminated land assessment will also be shown to require an understanding of the underlying chemistry when interpreting results.

However, at times, contamination profiles which appear to be straightforward at first glance can turn into complex situations that take longer than expected to resolve. Chemistry may or may not assist in such circumstances.

CHIRAL IMAGING WITH LUMINESCENT EUROPIUM COMPLEXES

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Highly emissive, lanthanide complexes based on polyaza-macrocyclic ligands with an integral sensitiser have been used extensively *in vitro* as analytical probes and *in cellulo* to stain cell compartments or study biological function. They are bright, possess long-lived, sharp emission bands and exhibit high photostability, and have been used to assess pH, pM and pX. [1] Such favourable photophysical properties make them promising candidates for other applications, such as security labelling.

The Δ and Λ enantiomers of 9-coordinate europium complexes have been resolved by chiral HPLC. Each enantiomer gives rise to mirror image circularly polarised luminescence (CPL) and is stable to racemisation under ambient conditions. Simple methods of detection of the resolved complexes have been developed, using band pass filters attached to a commercially available DSLR camera or CCD detector. Chiral image contrast has also been explored in microscopy, selecting the sign of the circularly polarised light, over a given wavelength range. [2] The resolved complexes show differential uptake and staining of cell organelles in living NIH 3T3 cells: the Λ isomer going to mitochondria the Δ mainly stains the lysosomes. The origins of the observed enantioselectivity require consideration of chiral recognition both in cell surface recognition during macropinocytosis and in differential transport rates by recycling vesicles.

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Cis resveratrol optical chirality: Towards optical detection of cellular stress response

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ABSTRACT

Resveratrol , a stilbenoid phytoalexin, has attracted interest due to evidence of beneficial health effects[1]. Resveratrol can exist in *trans (E)* or *cis (Z)* diastereomeric forms. Biological activity has been attributed to the *trans* form. It has been found that *cis*-resveratrol binds human tyrosyl tRNA synthetase, initiating downstream stress-related response[2]. The synthetase binds *cis* resveratrol more strongly than tyrosine. A binding-dependent conformational change may couple stabilization of *cis* resveratrol to activation of the stress response. We offer a comparative study of *cis* and *trans* resveratrol, using density functional theory calculations. *Cis* resveratrol is non-planar due to inter-ring steric clashes, introducing "handedness" to the molecule, which manifests as weak atropisomerism. We calculate the vibrational circular dichroism (VCD) and Raman optical activity (ROA) spectra of *trans* and *cis* forms, and show that *cis* resveratrol displays a chiral optical response. C*is* resveratrol solutions should be racemic mixtures, but only one atropisomer is observed in the co-crystal structure of resveratrol-bound tyrosyl tRNA synthetase. Our results suggest that enhancement of chirality indicated in the VCD and ROA spectra may be used for sensing of resveratrol-bound synthetase, indicating activation of the downstream stress-response.

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Combined fluorinated polymer and poly-L-lysine dendrimer as new potential contrast agents for magnetic resonance imaging ^{19}F

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Early diagnosis of diseases, including tumors, is the ultimate goal of biomedical imaging. Magnetic resonance imaging (MRI) is a technique for non-destructive and non-invasive diagnosis of a number of diseases including cancer. However, early detection of such diseases requires techniques with higher sensitivity, while maintaining high specificities for cancerous or diseased cells. The use of contrast agents improve the image quality and hence lead to a significant improvement in image analysis which in turns leads to more reliable/sensitive diagnosis. Recently, contrast agents bearing ^{19}F have been introduced as an attractive alternative to purely hydrogenated compounds, because unique spectroscopic signature leads to a high signal to noise ratio.[1] However promising these new fluorinated compounds are, their tendency to aggregate and the low mobility of fluorinated chains in physiological media have known to limit the sensitivity of ^{19}F MRI for clinical applications. In this work we propose overcoming this problem by creating new materials which can act as contrast agents. These will be based on a dendrimer containing ^{19}F that are soluble in water and can be readily functionalized to enable targeting. This represents a key objective in the advancement of MRI research.

The hyperbranched fluoropolymers used in this study belong to a class of tree-like synthetic macromolecules called dendritic polymers. They are polymers with a densely branched structure and hence a large number of end groups which provide multiple sites for functionalization which can be used for targeting.

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COMPARISON OF SCIENCE TEACHERS' OVERSEAS VOLUNTARY ACTIVITIES BY ACTIVITY THEORY

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ABSTRACT TEXT

The purpose of this study is to compare two overseas voluntary activities by Cultural Historical Activity Theory (CHAT). In 2016 Korean in-service science teachers went to Timor-Leste to run a teacher education program, and in 2017 Korean pre-service science teachers went to Nicaragua to teach elementary and secondary students. The CHAT is the tool of analyzing a human activity to find the whole structure of the activity and to reveal the conflicts among the elements of the activity that drive the development of the activity. The six elements of the activity system are subject, object, tools, community, rule, and division of labor. Two authors performed a participant observation of two voluntary activities, gathering data for the analysis. As a result, we found the differences in the contents of six elements of two activity system. For the conflicts we found both similarities and differences in two activity system. The subjects of two voluntary activities suffered from the language (that is, the conflict between the elements of subject and tool), e.g., tetum and español. In contrast, the pre-service science teachers experienced difficulty in teaching science to students (the conflict between subject and object) while the in-service science teachers had little difficulty in science teacher education. We could reconfirm the importance of community in a activity system. Especially the 'contact person' in the foreign country played a crucial role for the success of the voluntary activity. We will discuss the usefulness overseas voluntary activities for the science teacher education.

Complex Molecular Transformations in Fly Ash and Slag Based Matrices

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ABSTRACT TEXT

Solid-state NMR based techniques are a powerful tool to elucidate complex molecular structural transformations in disordered systems. One such class of materials are alumino-silicate binder matrices (cements) derived from industrial waste by-products such as fly ash (FA) and blast furnace slag (BFS). FA and BFS are candidates for "green" cements, due to their low energy consumption and CO_2 emissions. Upon activation by alkaline solutions, BFS and FA undergo a geopolymerization hydration reaction to form the hardened paste that can substitute ordinary cement. However BFS and FA exhibit significant differences in their mechanism of hydration and resultant chemical structures. Here, we show how a diverse set of advanced NMR spectroscopy techniques, enables us to uncover the rich structural chemistry of these highly disordered materials. Coupling quantitative ^{29}Si NMR with ^{27}Al multiple quantum magic angle spinning (MQMAS) NMR measurements at a high magnetic field (16.4 Tesla), provides information on the distinct silicate and aluminate chemical environments formed in the FA and BFS materials. Novel use of ultrafast-MAS NMR is demonstrated to identify formation of distinct structural domains within the hydrated matrices. The key finding is the use of 2D dimensional heteronuclear correlation spectroscopy, for the first time, to enable the characterization of the interactions and proximities between the distinct silicate, aluminate and Na^+ species within the three dimensional geopolymer network.

The methodologies presented here have a high applicability for the study of materials such as amorphous catalysts, zeolites and disordered glasses.

COMPUTATIONAL THINKING IN THE CHEMICAL SCIENCES

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ABSTRACT TEXT

Technology-led disruption of the workforce is a pressing issue for future employability [1], with up to 40% of the Australian workforce at significant risk of automation or mechanisation in the next 20 years. Chemists face a relatively small 10% chance [2] of digital disruption, however we must focus on skills to best equip chemistry graduates for this new employment landscape.

We believe that all chemistry graduates should be innovators and creators, not mere consumers, of digital, technological and mechanical advancements, and to do this requires high levels of computational and data analysis skills. This requires a curriculum that supports algorithmic and systems literacy and fluency that will enable full participation in the future global workforce. Computational thinking is the cognitive process that permits the representation of solutions in ways that can be coded, analysed, visualised and interpreted [3]. We will focus on the application of 'computational thinking' in the chemical sciences, giving relevant examples of its application in our context and charting its development throughout the curriculum.

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Conformational Control by Stereospecific Fluorination for Enhanced Protein Specificity

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ABSTRACT TEXT

Specificity of molecular recognition in the active site of a protein target is of general interest to drug discovery and medicinal chemistry. Fluorine is a chemical and conformational tuning handle with unique properties and has recently seen wide applications in controlling recognition specificity in protein-ligand interactions. Here stereospecific fluorination reactions have been developed to fluorinate seven-membered N-heterocycles frequently used as bioactive epitopes. These fluorinated N-heterocycles are then further transformed into natural product derivatives to target the nucleotide-binding site of the AGC protein kinase family. Enhanced isozyme specificity for some PKC isozymes can be achieved under the influence of single fluorine substitution. Structural homology models are used to ascertain potential protein-ligand interactions that give rise to specificity enhancement in the active site. Given that many drugs target nucleotide-binding pockets, this fluorine-based shape controlling approach may offer additional avenues of selectivity optimization, particularly for highly homologous active sites.

Conjugated Polymers for OPV and OTFT Applications

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ABSTRACT TEXT

Polymer solar cells (PSCs) are a promising alternative for clean and renewable energy due to their potential to be fabricated onto large area, light-weight flexible substrates by solution processing at low cost. Our recent progress in the molecular design of p-type conjugated polymers containing multi-fused ladder-type structure and the n-type fullerene derivatives containing cross-linkable styryl or epoxy groups will be presented. Both ladder-type conjugated polymers and n-type fullerene derivatives are used to fabricate high efficient bulk heterojunction PSCs. The cross-linkable fullerene derivatives are also used to fix the morphology of bulk heterojunction (BHJ) layer so as to improve the stability of PSCs. Recently a series of novel DA copolymers were developed by utilizing pyrene-modified porphyrin as complementary light-harvesting unit (LHU). It was found that adding proper amount of the LHU increased light absorption in the 400-500 nm region, rendering the porphyrin-incorporated D-A copolymers (PPor) panchromatic light absorbers. Voc-Jsc trade-offs commonly seen in many D-A polymers were not found in the PPors reported in this work. This is attributed to the presence of the LHUs increasing the Jsc without sacrificing the Voc and FF of the polymer solar cells (PSCs). Thus, 8.6% PCE was observed for the PPor: PC71BM single-junction PSCs. Furthermore, both fullerene and non-fullerene derivatives were also used as acceptors in this system to fabricate PSCs with a PCE more than 10 %.

CONTROL OF MARINE EMISSIONS IN PEARL RIVER DELTA REGION, CHINA

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ABSTRACT

In Hong Kong, after our efforts to tackle land-based emission sources including power plants and motor vehicles over the years, vessel emissions have now become the largest air pollution source, accounting for 44%, 33% and 36% of the total sulphur dioxide, nitrogen oxides and respirable suspended particulates (PM_{10}) respectively in 2014.

With the support from the local shipping industry, the Government of Hong Kong has taken a series of initiatives to reduce emissions from the marine sector in recent years.

To reduce emissions from local vessels, we introduced a regulation in April 2014 reducing the sulphur content of locally supplied marine light diesel from 0.5% to 0.05%.

Ocean going vessels are the major contributor of emissions in the marine sector. Following a voluntary fuel switch programme initiated by the shipping trade in 2011, the Government has enacted a regulation in July 2015 mandating ocean going vessels to switch to clean fuel while berthing. Hong Kong is the first city in Asia mandating the fuel switch requirement for ocean going vessels. Key findings in terms of atmospheric chemistry before and after the implementation of marine emissions control regulations will be highlighted. At the regional level, we are also collaborating with Mainland China authorities on the setting up of a Domestic Emission Control Area in the Pearl River Delta waters under a national marine emission control action plan issued by the Ministry of Transport in December 2015.

Controlled Synthesis of Functional Macrocyclic Poly(α-chloro-ε-caprolactone-co-ε-caprolactone) by Intramolecular Cycloaddition

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ABSTRACT TEXT

Much attention was paid to cyclic polymers and much effort was devoted to their design and synthesis for the last decades because of distinct properties compared to the linear counterparts, such as glass transition temperature, order-disorder transition, hydrodynamic volume and intrinsic viscosity. However, the quest for a general and effective concept of cyclization of high molecular chains under non very demanding conditions remains highly desirable and challenging. This work reports on a novel strategy for the synthesis of functional macrocyclic Poly(α-chloro-ε-caprolactone-co-ε-caprolactone) of high molecular weight (Mn = $3.5\text{x}10^4$ g mol^{-1}, $F_{\alpha\text{Cl}\varepsilon\text{CL}}$ = 0.18). It relies on the intramolecular cyclization by cycloaddition of a few acrylic unsaturations in the very close vicinity of the propagating sites of chains synthesized by ring-opening polymerization initiated by a cyclic tin(IV) dialkoxide. Remarkably, the concentration of the chains ($3.0\text{x}10^{-2}$ M) at which the cyclization has been carried out, is at least three order of magnitude higher compared to cyclization of linear precursors ($<10^{-5}$ M). No linear species is ever involved in the polymerization and permanent cyclization steps, which allows higher molecular weight macrocyclic aliphatic (co)polyesters to be prepared with high efficiency. Moreover, the propagating tin(IV) dialkoxide remains active after cyclization and paves the way to further derivation and macromolecular engineering. In addition, the functional chloro groups of the macrocyclic copolyesters prepared herein can be further modified by grafting from/onto technologies to achieve novel architectures based on macrocyclic building blocks. The thermal properties of the cyclic copolyesters and the precursors were analyzed by differential scanning calorimetry.

CONTROLLING AND PREVENTING OXIDATION OF SILICENE NANOSHEETS

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ABSTRACT

The investigation of two-dimensional (2D) nanomaterials has become one of the most quickly growing areas in science due to their unique properties and ability to form layers in various electronic devices. Silicene, composed solely of Si atoms arranged in a hexagonal honeycomb network [1], is one of the most promising 2D nanomaterials as it is highly compatible with existing electronic devices. Its widespread application is, however, currently hindered by its instability in air.

Using density functional theory and *ab initio* molecular dynamics simulations, we have shown that oxidation of silicene supported on a Ag(111) substrate can easily take place either at low or high oxygen doses [2,3]. Further the extent of oxidation can alter the electronic properties and hence control of the process is highly desirable so as to obtain non-oxidized, partially-oxidized, or fully-oxidized silicene. Our most recent work has shown that by placing silicene between planar crystals of calcium fluoride and calcium disilicide, it is possible to obtain a wavy bilayer form of silicene that is highly resistant to oxidation [4].

These findings are beneficial to the current drive for fabrication of smaller and thinner electronic devices, batteries and gas sensors.

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Controlling Gold Nanoparticle Deposition on Large Zinc Oxide Nanoparticles

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This talk outlines our group's investigations into the synthesis of coupled semiconductor-metal nanoparticle systems. We have applied both solvothermal and photochemical colloid synthesis techniques to fabricate stable, monodisperse zinc oxide nanocrystals and composite zinc oxide – gold nanoparticle structures with different morphologies. Seed-assisted crystal growth techniques have been used to generate Au-ZnO nanoparticle dimers, as well as trimers, nanocrystal tetramers and oligomers, where the seeded ZnO nanocrystals form hexagonal pyramids. The Au crystal seed size was also observed to play a crucial role in determining the final product's form. HRTEM revealed details of the epitaxial lattice matching of the two component materials by this synthetic route. This growth of ZnO crystals on Au seed particles changes the frequency of the Au localised surface plasmon resonance absorption of the multicomponent system. Alternatively, photodeposition of Au onto ZnO nanoparticles generates composite hybrids where Au nanoparticles attach to individual ZnO nanocrystals. Our results indicate that understanding how to control rates of interfacial electron transfer at the solid-solution interface and the accumulation of charge within the inorganic semiconductor nanocrystal can prove particularly useful when trying to generate different types of photodeposited heterostructures. Rates of interfacial electron transfer can be adjusted by changing solvent permittivity, viscosity and levels of dissolved oxygen in the colloid system. Our attempts to fabricate Au-ZnO heterostructures with precise spatial-coupling between photodeposited gold nanoparticles indicate that the chemical form of the Au precursor salt and the time of UV irradiation exposure have a strong influence over the pattern of gold nanocrystal nucleation.

Controlling the Deep-Red Emission in Dinuclear Platinum(II) Complexes

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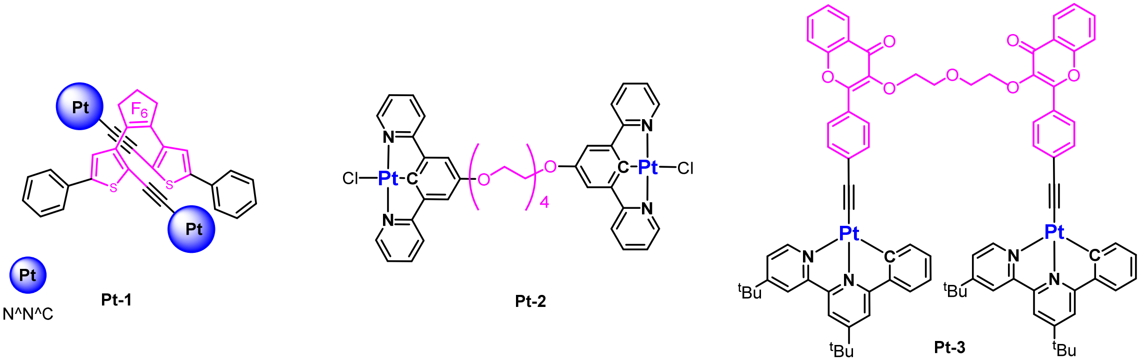
Cyclometallated Pt(II) complexes have received much attention in recent years due to their strong luminescence properties, driven especially by their potential applications in opto-electronic devices. Importantly, their square planar geometry facilitates interfacial interactions either in the ground state (e.g. aggregation) or in the excited state (e.g. excimer formation). Numerous examples of aggregation and excimer formation have been reported for mononuclear Pt(II) complexes with tridentate cyclometallating ligands, taking advantage of their propensity to develop π-π and Pt…Pt interactions.[1] By linking together two cyclometallated complexes, in order to promote face-to-face intramolecular interactions, intense luminescence in the red region of the spectrum could be achieved. We have used this approach to investigate new routes to deep-red triplet emitters in solution.

We will report on the synthesis and spectroscopic properties of new dinuclear Pt(II) complexes **Pt-1-3** with N^N^C- and N^C^N-coordinating ligands where the two Pt units are linked by various -rigid or flexible- bridges.[2]



Molecular structures of the studied dinuclar cyclometallated platinum complexes

We will show how the emission properties are affected by the nature of the linker group and temperature, solvent, and metal-ion-binding.

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CONVERSION OF IRON ORE INTO AN EFFICIENT WATER SPLITTING ELECTROCATALYST

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The storage of intermittent renewable energy sources is now a key issue for developing new functional materials. Earth-abundant transition metal based catalysts have been investigated for their applicability in water electrolysers as a means to store electricity in the form of hydrogen. A key bottleneck however is developing a catalyst that is active for the oxygen evolution part of the water splitting reaction. Here we report a novel electrochemical approach to synthesise a highly active catalyst based on iron oxide for the oxygen evolution reaction (OER). Iron ore is used as the iron oxide source and nickel is doped into the structure via an electrochemical process to form Ni-Fe oxide catalysts. This material achieved a current density of 10 mA/cm^2 at a low overpotential of only 270 mV and maintained its activity for extended periods of electrolysis under alkaline conditions. It was further confirmed that this robust electroactive catalyst performed for several weeks without any degradation in performance. This simple process to convert a readily available Australian commodity into a value-added product may be of considerable interest.

CU-INDUCED CHANGES IN INTRACELLULAR THIOLS IN MARINE MICROALGAE

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ABSTRACT

Toxicity of metals to aquatic organisms is dependent on both external factors, such as exposure concentration and water quality parameters, and intracellular processes including specific metal-binding sites and detoxification. Current models used to predict copper (Cu) toxicity in microalgae do not effectively consider the intracellular processes. This research examined the toxicity of Cu towards microalgae by investigating (i) the cellular distribution and co-localisation of metals (synchrotron); (ii) intracellular Cu-binding ligands (phytochelatins and glutathione) in four species of marine microalgae exposed to Cu at their respective IC50 (concentration of Cu required to inhibit population growth by 50%) at intervals over 72-h.
Despite similar Cu tolerances in the diatoms *Phaeodactylum tricornutum* and *Ceratoneis closterium*, differences in internalised Cu, phytochelatin production and reduced glutathione were observed. *P. tricornutum* internalising significantly less Cu but produced more phytochelatins and of longer chain length than *C. closterium*. Two green algae, *Dunaliella tertiolecta* and *Tetraselmis* sp. had very different Cu tolerances, and also exhibited differences in internalised Cu, phytochelatin production and reduced glutathione concentrations. *Tetraselmis* sp. internalised three times more Cu than *D. tertiolecta* and had significantly more intracellular thiols. Phytochelatin production was markedly different between acute (< 24 h) and chronic exposures (24 – 72 h), with shorter chain lengths dominating for chronic exposures.

This work has shown that the intracellular reaction to Cu is species specific, and responses were not necessarily related to their respective tolerances, or the amount of intracellular Cu. This suggests that there may be multiple modes of Cu toxicity and that detoxification processes vary between species.

Crown ether nanosensors for the rapid in-field detection of heavy metals

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ABSTRACT

Due to the adverse effects posed by mercury and lead pollution, there are constant demands for selective, sensitive, cost effective and field deployable methods for their detection. Crown ethers form highly stable and selective complexes with many metals because of their ability to act as ionophores. Therefore they can be used as highly efficient recognition molecules for metal ion detection. In this work, 4 - aminobenzo-18-crown-6 and 4-aminodibenzo-18-crown-6 were used to develop sensitive and selective nanosensors for the rapid detection of Hg(II) and Pb(II) pollution by surface enhanced Raman spectroscopy (SERS). The crown ethers were used to spontaneously form aqueous complexes with the target metal ions in water. The complexes were rapidly immobilized onto a nanostructured gold substrate and screened by a handheld Raman spectrometer. Ultraviolet and fluorescence spectroscopy were used to confirm the complex formation between the crown ethers and the target metal ions. The new nanosensors selectively detected Pb(II) and Hg(II) in water in the presence of other environmentally relevant metal ions such as Cu(II), Ca(II), K, Ba(II), Li, Ni(II), Co(II) and Na(I). The limit of quantification (LOQ) for Hg (II) and Pb(II) by the new nanosensors were 2.07pM and 4.81pM for Hg (II) and Pb (II) respectively. These are lower by several orders of magnitude than the World Health Organisation permissible levels of these metals in drinking water. Due to its high portability, selectivity and sensitivity, the new nanosensing method has strong potential for the rapid in-field screening of heavy metal pollution in water.

CYBERTONGUE® for Food and Health – A BRET based microfluidic sensing platform.

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Abstract

Objective quantitative measures of chemical composition are invaluable in many spheres of human activity, from healthcare to industrial processing. A number of very sophisticated analytical methods have been developed, for separating and identifying chemicals, including chromatography and mass spectrometry. The sensitivity, resolving power and user-friendliness of these technologies are spectacular. However, these existing methods are, in general, expensive, slow and not very portable. They may generate large amounts of data, requiring time and expertise to interpret. Therefore they have not been widely adopted outside research or analytical laboratory environments. To allow chemical analysis to be easily carried out in "real world" situations, there is a need for faster and more portable methods that can be used by non-specialists. Highly evolved chemical senses are critical for the survival of most modern day organisms. We have drawn inspiration from biological systems to develop a sensitive, fast and easy-to-use chemical analyser. The CYBERTONGUE® biosensing platform can measure a wide range of analytes, continuously and rapidly. The platform's essential features are that: (1) it uses bioluminescence resonance energy transfer (BRET) as the transduction modality; (2) it incorporates multiple classes of biological recognition elements and, within each class, many variants are possible; (3) it works in the fluid phase of a multiplexed microfluidic system. Currently the system can measure several volatile organic compounds, using olfactory receptors from nematode worms, three different types of proteolytic enzymes using engineered peptide substrates and a number of different disaccharides using a bacterial periplasmic binding protein.

DEAROMATIVE [3+2] CYCLOADDITION REACTIONS TOWARDS POLYCYCLIC HETEROCYCLES

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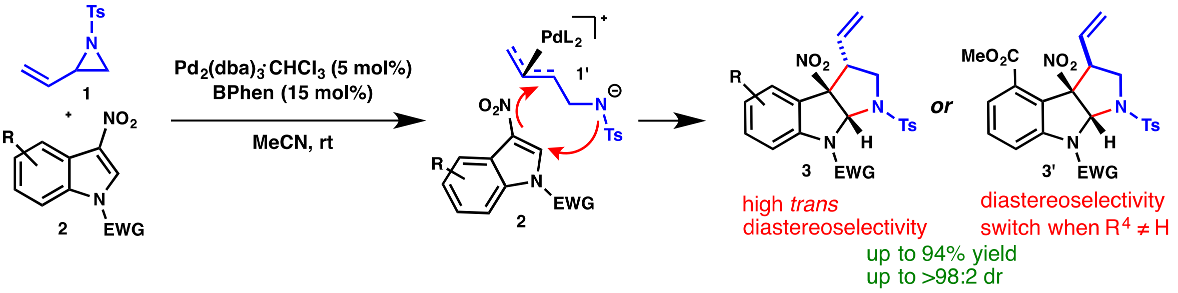
The [3 + 2] cycloaddition reaction of nitrogen-containing 1,3-dipoles with electron deficient olefins is an efficient method for the synthesis of pyrrolidine-containing compounds.[2] Less studied however, is the combination of zwitterionic 1,3-dipoles derived from vinyaziridines in combination with electron-deficient indoles in [3 + 2] dearomative cycloaddition reactions. We will present our results[3] showing that palladium(0)-catalysts can reveal a zwitterionic 1,3-dipole **1'** from *N*-tosyl-vinylaziridine **1** that can undergo a cycloaddition with highly electron-poor 3-nitro-indoles **2**. This reaction generates the biologically relevant and synthetically versatile pyrrolo[2,3-b]indole **3** moiety in a single operation. The reactions proceed to give the *trans* diastereoisomer with high selectivity, however, when a 4-substituent is present on the indole ring a complete reversal of diatereoselectivity is observed.



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Describing the Reflection System for R-IR-MSP Analysis of Vehicle Paints

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Modern vehicle paint systems are complex combinations of pigments, binders and additives, with different formulations layered to create a final finish. Tricoat systems are the most common layer structure in new vehicles, including multiple primers, covered by a coloured basecoat, covered with metallic or pearlescent pigments, finished with a glossy clearcoat.

Vehicles, paints and paint flakes are often used as evidence in forensic investigations, particularly to link paint to a vehicle of interest. A typical forensic analysis procedure involves carrying out a combination of tests, chemical and physical, that attempt to identify the chemical composition and colour properties of the paints. Infrared spectroscopy is often used to characterise organic binders and minerals in paint as it is quick, non-destructive and sensitive to molecular structure.

This research has focused on developing reflection infrared micro-spectroscopy (R-IR-MSP) as a technique for the identification and analysis of vehicle paints. Due to the layered structure of bulk vehicle paint samples, reflection measurements of these coatings often mimics transflection rather than straightforward reflection and shows the effects of several phenomena that mask the expected spectral features. Thus, in order to accurately interpret and understand the resultant spectra, the reflection system for vehicle paints needs to be described. This has been achieved, qualitatively, through the investigation and identification of spectral features and has lead to the development of a previously reported algorithm for the removal of reflection effects from R-IR-MSP spectra.

Design of Collagen-Mimetic Peptides to Fold AAB-Type Collagen Heterotrimers

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ABSTRACT

Many natural collagens are heterotrimers composed of two (AAB) or three (ABC) different peptide chains, and thus heterotrimeric constructs are more desirable for mimicking such collagens. Exploring the forces to assemble synthetic collagen-mimetic peptides (CMPs) into heterotrimers has been an attractive topic in preparing collagen-related biomaterials. We designed and synthesized two cationic CMPs (CR and CK) in which multiple Arg or Lys residues are installed in their C-terminal region, and one aromatic CMP (CF) whose C-terminal end contains multiple Phe residues. Circular dichroism and NMR spectroscopy showed that both CR-CF and CK-CF mixtures could produce AAB-type heterotrimers, suggesting that the C-terminal cation–π interactions between cationic and aromatic residues could serve as a nucleation force to induce the folding of heterotrimers. In particular, only one major heterotrimeric fold was found in each mixture. For CR-CF mixtures, either the heterotrimer with two CR chains and one CF chain or that with one CR chain and two CF chains could form, depending on the molar ratios of CR to CF in solution. In contrast, in CK-CF mixtures only the heterotrimer consisting of two CK chains and one CF chain was found in solution even increasing the ratio of CF, implying that the heterotrimer composed of one CK chain and two CF chains is too unstable to form. Differential scanning calorimetry analysis further showed that the folding of these heterotrimers is governed by entropic effects. Our results provide a new design to prepare AAB-type collagen heterotrimers and reveal new insights into their folding thermodynamics.

Design of Polysulfides Trapped Separator for High-Energy-Density Li-S Batteries

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ABSTRACT TEXT

In this work, the light-weight and scalable organic macromolecule, graphitic carbon nitride ($g\text{-}C_3N_4$) with enriched polysulfides adsorption sites of pyridinic-N, was introduced to achieve the effective functionalization of separator at the molecular level. This simple method overcomes the difficulty of low doping content as well as uncontrolled existence form of nitrogen heteroatom in the final product. Besides the conventional pyridinic-N-Li bond formed in the vacanies of $g\text{-}C_3N_4$, the C-S bond was interestingly observed between $g\text{-}C_3N_4$ and Li_2S, which endowed $g\text{-}C_3N_4$ with the inherent adsorption capacity for polysulfides. In addition, the micro-sized $g\text{-}C_3N_4$ provided the coating layer with good mechanical strength to guarantee its restriction function for polysulfides during long cycling. As a result, an excellent reversible capacity of 840 mA h g^{-1} was retained at 0.5 C after 400 cycles for pure sulfur electrode, much better than that of the cell with innocent carbon-coated separator. Even at current density of 1 C, the cell still delivered a stable capacity of 732.7 mA h g^{-1} after 500 cycles. Moreover, when further increasing the sulfur loading to 5 mg cm^{-2}, an excellent specific capacity of 1134.7 mA h g^{-1} was acquired with the stable cycle stability, ensuring a high areal capacity of 5.11 mA h cm^{-2}. Besides the intrinsic adsorption ability for polysulfides, the $g\text{-}C_3N_4$ is non-toxic and mass-produced. Therefore, the scalable separator decorated with $g\text{-}C_3N_4$ and commercial sulfur cathode promise the high energy density for the practical application of Li-S batteries.

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DESIGNED IONIC LIQUIDS TO INVESTIGATE PROTEIN SELF-ASSEMBLY, STABILITY AND ACTIVITY IN A QUANTITATIVE AND SYSTEMATIC MANNER TO CONTROL THE 3-D STRUCTURE AND FUNCTION OF PROTEINS

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ABSTRACT

Ionic liquids (ILs) can have a stabilizing or destabilizing effect on proteins, which is strongly dependent on the cation and anion of the IL. The ILs can be chosen and tailored to serve as a beneficial solvent for enzymatic reactions, protein storage, and other protein based applications. Aqueous solutions containing ILs have successfully been used to stabilise, crystallise, denature, and form Amyloid fibrils of various proteins. The aim here is to develop detailed structure-property relationships between different protic ionic liquid cations and anions and their ability to stabilize proteins. This will advance our understanding of specific solvent properties on protein stability, such as cation, anion, ionic strength, salt concentration and pH. The proteins of primary interest are water soluble proteins which are enzymes, whose functionality is dependent on their 3-D structure. Our group has recently explored the protein-IL interactions for lysozyme in four protic ionic liquids (PILs). Here we extend that research to Lysozyme, Trypsin, Amylase and Beta-Lactoglobulin in 8 alkylammonium PILs, in aqueous and non-stoichiometric PIL solutions. This resulted in over 1000 samples, which were characterized using small angle X-ray scattering (SAXS), IR, DSC and activity assays. The radius of gyration (R_g) and Kratky plots from the SAXS data were used to screen the data to determine under which conditions the proteins were likely to be folded. This work will enable the role of different ions, pH and ionicity in PIL solutions to be determined for different proteins, and has implications for the pharmaceutical and industrial applications

Designing Fluorescent Tools To Probe NK$_1$R Signalling From Endosomal Platforms

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The recent identification of endosomal-propagated signalling in select G protein-coupled receptors, known as the signalling endosome hypothesis,[1] has broadened our view of the complexity of receptor signalling mechanisms that occur post receptor activation. However, the precise mechanisms by which endosomal signalling occurs, as well as its functional significance and potential for therapeutic exploitation is currently unclear. To improve our understanding of these processes, we describe the design and synthesis of a series of fluorescent probes to investigate endosomal signalling by the Neurokinin1 Receptor (NK$_1$R), an important mediator of central pain transmission. Lipid tethered drugs are efficiently anchored into cellular membranes, which improves cellular uptake and promotes delivery into endosomes through constitutive internalisation processes.[2] We have previously shown that lipid-tethered antagonists have a greater capacity for blocking NK$_1$R-mediated signalling when compared to their soluble, non-lipidated counterparts, and this can lead to improved analgesic outcomes.[3] Our specific NK$_1$R probes incorporate spantide (a peptide-based NK$_1$R antagonist), cholestanol (a lipid raft anchor) and the near-infrared fluorescent dye Cy5 (for visualisation). Initial imaging has demonstrated, for the first time, that these cholestanol-conjugated NK$_1$R antagonists are rapidly delivered to NK$_1$R-positive endosomes (Figure 1). Subsequent analysis has confirmed probe-receptor interactions and the potential for these compounds to block signalling within endosomes or through inhibition of receptor internalisation. Furthermore, these probes will be advantageous in imaging-based assessment of lipidated drug uptake and tissue distribution in future studies.

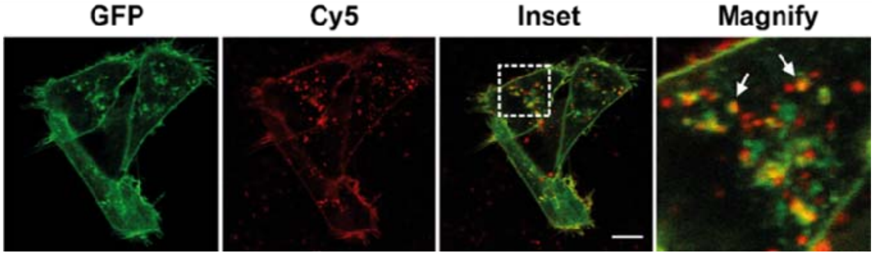

Figure 1. Fluorescence confocal microscopy demonstrates that fluorescent Cy5-Chol-Span probe (red) can target NK$_1$R-GFP fusion protein (green) within endosomes.

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Designing New Bio-Smart Materials Through Protein-Polymer Conjugates

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Hybrid materials combine multiple properties from diverse sources into the one system. Conjugating biomolecules (proteins and peptides) to synthetic polymers is a way of developing new hybrid materials that possess both synthetic and biological properties. Synthetic stimuli-responsive (e.g., pH) polymers that can form nanoparticles within biologically relevant conditions have potential applications in drug and vaccine delivery. However, these synthetic polymers alone do not have the specific targeting attributes seen in proteins such as antibodies or nanobodies. The conjugated protein/ peptide provides the necessary 'bio-smarts', giving the hybrid material functionality and allowing it to interact specifically with other biomolecules, thus improving cell targeting. Herein, we report the synthesis, functionalisation and bio-conjugation of the pH-responsive and self-assembling polymer poly[(2-(diethylamino) ethyl methacrylate)-co-(2- (diisopropylamino) ethyl methacrylate)-co-(2-(pyridyldithio) ethyl methacrylate)] (PDEA-co-DPA-co-PDS). A post-polymerisation functionalisation method was chosen to end-cap a dibenzocylooctyne (DBCO) reactive handle to the polymer RAFT group; allowing for the copper free 'click' conjugation of an azide-functionalised nanobody for cell targeting. Optimisation of this end-capping procedure was performed, through a mini throughput screen of coupling reagents and solvents, resulting in reasonable yields of DBCO-functionalised polymer, which could then be 'clicked' with targeting proteins. Subsequent hybrid conjugates were responsive to pH, and could assemble into nanoparticles (based on the synthetic pH responsive polymer), whilst displaying cell specific targeting from the protein component.

DESIGNING SUPERATOMIC ASSEMBLIES

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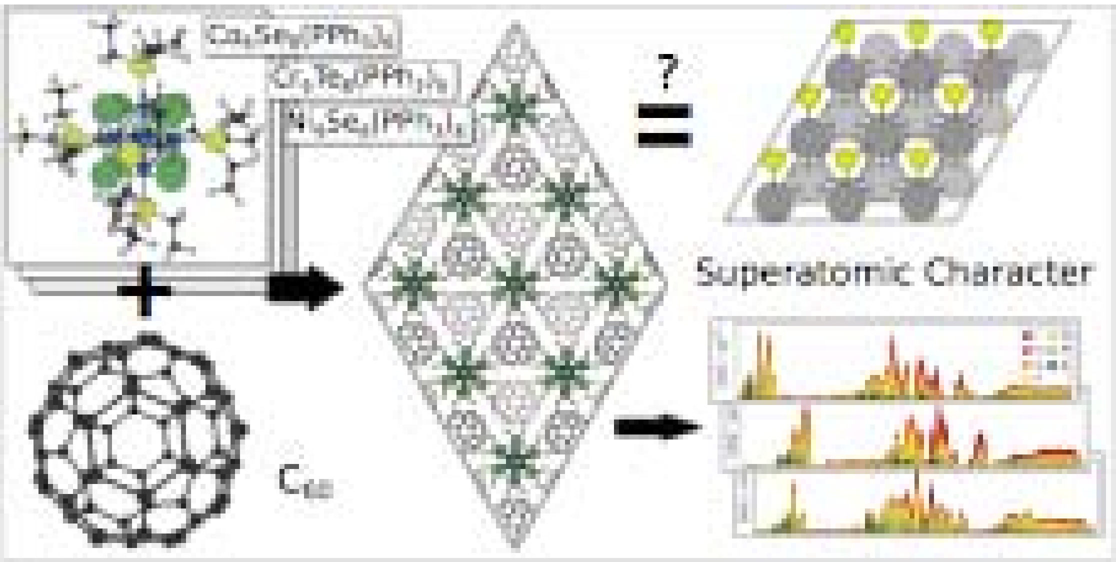
Inspired by recent progress in the synthesis of cluster assembled solids, and the theoretical description of globally delocalized electronic structure of nanoscale building blocks – superatoms – we address the question to what extent the three new materials $[Co_6Se_8(PEt_3)_6][C_{60}]_2$, $[Cr_6Te_8(PEt_3)_6][C_{60}]_2$, and $[Ni_9Te_6(PEt_3)_8]C_{60}$, upon forming bulk compounds, imitate atomic analogues. Although experimental results suggest the latter, a theoretical approach is the method of choice for offering a conclusive answer and for studying the actual superatomic character.

The concept of superatoms for describing atom-imitating clusters is very intriguing since it allows chemists to apply their chemical intuition – a useful tool for predicting new materials – when it comes to inter-cluster reactions. Thus, we systematically study the lattice structure, the intercluster binding, and the electronic structure by density functional theory and assess their superatomic features. We show that collective properties arise upon bulk formation, which promotes arguments for the formation of solids in which the constituent clusters have a superatomic character that determines some form of chemical bonding.

Finally, we present principles for the design of tunable superatomic assemblies, and methods for the prediction of their electronic properties.



Detection of 2,4,6-Trinitrotoluene (TNT) Using a Miniaturized, Disposable Electrochemical Sensor

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ABSTRACT

In this talk, we will demonstrate a new electrochemical method to detect and quantify the explosive compound 2,4,6-trinitrotoluene (TNT) in aqueous solutions. A disposable thin-film electrode modified with a droplet of a gel-polymer electrolyte (GPE) is immersed directly into samples of TNT at concentrations of 1–10 µg/mL. The GPE contains the hydrophobic room temperature ionic liquid (RTIL) trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([$P_{14,6,6,6}$][NTf_2]) and the polymer poly(hexyl methacrylate) (PHMA). The RTIL acts to preconcentrate TNT into the GPE, and provides ionic conductivity. The polymer provides both (i) sufficient viscosity to ensure mechanical stability of the GPE, and (ii) strong hydrophobicity to minimise leaching of the RTIL. Square wave voltammetry (SWV) on the first reduction peak of TNT-preconcentrated samples (15 minutes soaking with mechanical stirring), gave linear plots of peak current vs. cumulative concentration of TNT, and a limit of detection of 0.37 µg/mL (aqueous phase concentration). Additionally, the voltammetry of the first reduction peak of TNT in [$P_{14,6,6,6}$][NTf_2] was unaffected by the presence of oxygen – in contrast to that observed in an imidazolium-based RTIL – providing excellent selectivity over oxygen in real environments. The sensor device is able to quickly and easily quantify TNT concentrations at typical groundwater contamination levels. The low-cost and portability of the sensor device, along with the minimal amounts of GPE materials required, make this a viable platform for the onsite monitoring of explosives, which is currently a significant operational challenge.

Deuterium Labelling: A Tool for Structural Studies Of Multi-Component Systems

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Molecular deuteration of organic compounds is an essential prerequisite in many ^{2}H (deuterium) NMR, infrared, mass spectroscopy, and neutron studies. Despite this wide need, only limited global research initiatives in the field of deuterium labelling have been available, where the majority of these programs only focus on biological deuteration of proteins and lipids. This has restricted the experiments that can be performed, and formed a bottle-neck for advancing the applications.

In this paper we will discuss the recent advancements and the impact of deuteration on the research outcomes achieved by using deuterated molecules produced by the National Deuteration Facility of the Australian Nuclear Science and Technology Organisation. Recent high-impact case studies in the fields of molecular electronics, structural biology, and biotechnology will be presented which reveal the exciting and diverse characterisation studies which are now available. The chemical deuteration of ionic liquids, surfactants, sugars, heterocyclic and aromatic compounds has made possible a wide range of investigations. This includes the study of (i) the diffusion of organic films at interfaces in organic light emitting diodes (OLEDs) using neutron reflectometry[1] ii) the structure and host-guest properties of metal-organic frameworks (MOFs) using neutron diffraction[2] iii) the digestion of medium chain triglycerides using selective deuteration, mass spectrometry and NMR.[3]

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Development and application of mesoporous polymer monolith for sample preparation

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ABSTRACT

Monolithic porous polymeric materials have made several advancements in analytical and separation science by quantifying certain compounds from different sample matrix such as environmental, food, biological, bio-clinical or pharmaceutical sectors. We report the synthesis, characterisation and application of a novel mesoporous polymer monolith as a suitable sorbent for solid phase extraction (SPE) of small molecular weight compounds below 500 Da. To characterise the porous structure, the materials were studied by scanning electron microscopy (SEM) and by gas physisorption analysis. The SEM images exhibit a clustered globular morphology which is similar to an organic polymer monolith and the nitrogen adsorption-desorption isotherm indicates the presence of mesopores with an average pore size of 3 nm and a high surface area of 606 m^2/g. A quantitative analysis was conducted by using different molecular weight synthetic peptides from 300-700 Da to find the optimum adsorption capacity of the monolith material by reversed-phase high performance liquid chromatography (RP-HPLC). The results reveal the novel monolith has an optimum binding capacity of 250-100 mg/g and an excellent recovery of 100-50% of analytes within a cut off of 500 Da compared with the commercially available polymeric SPE resins. The application of the novel monolith material is targeted on the extraction of perfluorinated compounds from environmental matrices. Therefore, this novel monolith material can be considered as a prospective sorbent for the extraction and purification of small analytes in various fields, with an improved selectivity, high adsorption capacity and mechanical stability.

Development and Assessment of Professional Skills in First Year Chemistry

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Students in first-year chemistry classes come from a variety of backgrounds, with many students unaware of the qualities and behaviours of a professional scientist. Throughout their degree, students will gradually develop their cognitive skills, but they are not adequately taught or assessed on their professional behavioural skills as scientists. In order to assist students with their transition into university, while also preparing them for their eventual transition into the workforce, it was beneficial to embed professional identity from the very first semester. To boost the student's awareness of building a professional identity as scientists in a laboratory setting the professional practice assessment was developed (Professional Practice Points (PPP)). The skills that were assessed included organisation, work-related skills and communication. By engaging students with professional behaviours and what it means to be a scientist during their first semester, students are able to build on this foundation of professional identity throughout their undergraduate degree. Students were able to self-assess their performance at the end of each laboratory class and be provided with individualised feedback on their professionalism in the laboratory by our teaching staff. This activity was received positively by students and staff with over 50% of students believing it increased their confidence in the laboratory and helped them to better understand the expectations of them as students. Staff also saw a significant improvement in student behaviour and engagement because of this activity, creating a more professional and positive lerning environment.

Development and biological evaluation of a photoactivatable small molecule microtubule-targeting agent

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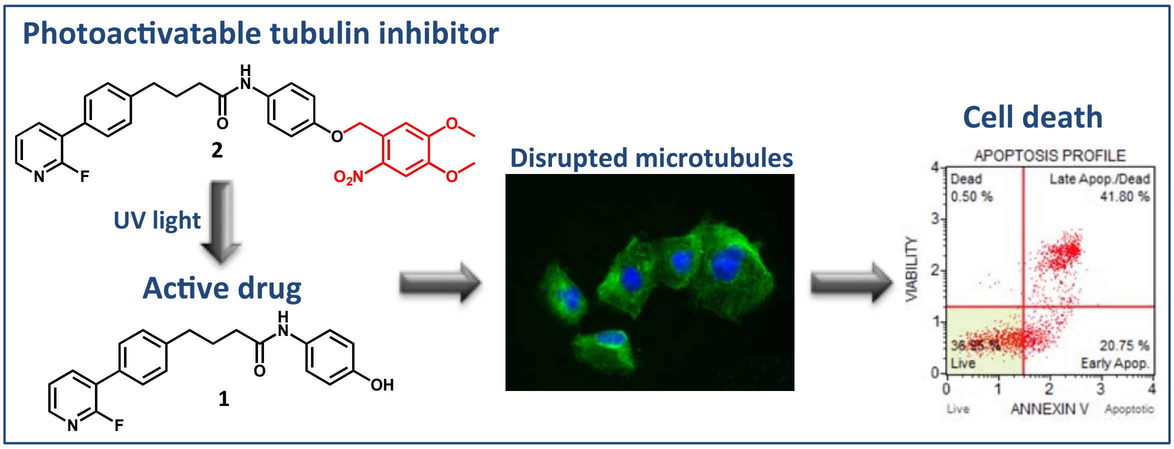
Photoremovable protecting groups added to bioactive molecules provide spatial and temporal control of the biological effects. We will present synthesis and characterization of the first photoactivatable small-molecule tubulin inhibitor. By blocking the pharmacophoric OH group on compound **1**, that binds into the colchicine binding site on tubulin, with photoremovable 4,5-dimethoxy-2-nitrobenzyl moiety we developed the photocaged prodrug **2** that had no effect in biological assays. Short UV light exposure of the derivative **2** or UV-irradiation of cells treated with **2** resulted in fast and potent inhibition of tubulin polymerization, attenuation of cell viability and apoptotic cell death, implicating release of the parent active compound. This study validates for the first time the photoactivatable prodrug concept in the field of small molecule tubulin inhibitors and the caged derivative **2** represents a novel tool in anti-tubulin approaches.



Development and Process Validation of [18F]GE-216 on FASTlabTM Synthesizer; A Radiotracer for Imaging Tau Pathology.

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[18F]GE-216, also known as [18F]-THK5351, is an investigational PET radiopharmaceutical. Possessing high sensitivity and specificity for tau protein fibrils in the human brain, [18F]GE-216 imaging enables topographical mapping of brain tau loads and prognosis of Alzheimers and other neurodegenerative diseases. GE Healthcare have automated and optimised the synthesis of [18F]GE-216 on the FASTlabTM synthesiser, with SPE purification using a single-use cassette. Method transfer and in-house (Royal Brisbane and Women's Hospital) process validation was required prior to use of the tracer in clinical research.

Three development batches of [18F]GE-216 were prepared to investigate method transfer from GE to RBWH and establish the assessment criteria against which the process validation would be performed. The product was examined for bacterial endotoxin content, half-life, radionuclidic purity, product appearance, sterility, reaction yield variation, stability of formulation, radio/chemical purity by HPLC, residual solvent concentration by GCMS, pH, residual radionuclidic impurities and radioactive concentration. Having established the assessment criteria, a series of 3 consecutive process validation batches were performed to validate the production and QC methodology.

SPE purified [18F]GE-216 was prepared in an average radiochemical yield of 38 % (NDC) from 60 – 65 GBq [18F]-fluoride. The final formulation volume (41 mL) was obtained after 45 minutes and found to be clear, sterile, particulate and BET free, and radiochemically pure through 8 hours from the EOS. All attributes of the product passed the established assessment criteria.

Method transfer and validation successfully produced a sterile, endotoxin free radiopharmaceutical suitable for use in humans in clinical research.

Development of an Evidence Based "Certificate of Laboratory Teaching"

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The laboratory class is a unique learning environment with the potential to achieve an enormous number of theoretical and practical objectives. Subsequently, the demands on students and instructors are great. The students must not only learn manipulative techniques, but also link theory to practice, problem-solve, interpret data, interact with staff and other students, and successfully navigate the lab itself. Learning in this situation can be greatly assisted by an instructor who is able to guide students through this complex process. However, what are the skills and competencies required by laboratory instructors to effectively carry out these tasks? Effective teaching in a laboratory class is different from that of a regular classroom; for example, instruction in a laboratory class is generally more interactive and one-on-one than in a classroom.[1]

How can instructors in laboratory classes demonstrate that they are providing quality laboratory teaching, and what evidence should they provide as evidence? The UK Higher Education Academy Fellowships[2] recognise a commitment to professionalism in teaching and learning and the HEA Associate Fellow, while not specifically designed for laboratory instructors, is the most appropriate category for demonstrators. To increase the profile and benefits of quality laboratory teaching, in an Australian context, a framework for an evidence-based "Certificate of Laboratory Demonstrating" will be described.

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Development and validation of an extraction and quantification method for radiocaesium in seawater

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ABSTRACT

An automated unit was developed, for the in-situ extraction of radiocaesium (^{137}Cs and ^{134}Cs) from large volumes of seawater. The unit, purposely designed for field work, is housed in a strong case and is easy to transport and to operate. Four filter cartridges are connected in series; first two cartridges are used to remove any suspended material that may be present in the seawater, while the last two cartridges are coated with potassium copper hexacyanoferrate for caesium extraction. Once the extraction is completed, the coated cartridges are processed in the laboratory, and the radiocaesium quantified using high resolution gamma spectrometry.

The method was validated for the following criteria: selectivity, trueness, precision, linearity, limit of detection, traceability and robustness (using the Plackett-Burman experimental design). The validation showed the method to be fit for purpose and that changes in key experimental factors did not have a significant effect on the results.

This technique is able to achieve very low detection limits and has been used for monitoring of Australian ocean and coastal waters, including at ports visited by nuclear-powered warships. The results for the environmental measurements in Australian seawater correlate well with those reported in the Worldwide Marine Radioactivity Study (WOMARS)

DEVELOPMENT OF SILICA COATED FIBRE TECHNOLOGY (SiFT) FOR THE DETECTION OF PHARMACEUTICAL DRUGS

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The simplicity and flexibility of micro-extraction techniques - specifically "coated fibre" micro-extraction technologies – have recently expanded into the field of bioanalysis with less-invasive sampling *in vivo* and *ex vivo*. We have established a modified method to coat stainless steel fibres with a composite material composed of high purity silica particles embedded within a porous polymer matrix (SiFT). To evaluate the best stationary phase to coat the fibre we explored the selectivity of 6 stationary phases for the extraction of pharmaceuticals. The selected phases were 10 micron 120Å, methyl (C1), butyl (C4), phenyl (C6), octyl (C8), polymeric octadecyl (C18) and diol functionality. The C18, C8 and phenyl presented high selectivity and good retention properties and were selected as best suited stationary phases for fibre coating. Parameters that influence the optimal fibre coating were explored including slurry composition, speed of coating and polymerisation parameters. The composite is in the process of optimisation in terms of both binding capacity and binding kinetics and to increase the binding capacity of the fibre with smaller particles (3 micron 120 Å polymeric octadecyl (C18)) coatings also being under optimisation processes. The C18 coated SiFT could extract the pharmaceutical drugs diclofenac from an aqueous solution with a lowest concentration of 100pg/ml, and contented recoveries were attained by direct coupling with ESI-MS. The experimental results of this work will guide future developments in sample preparation methods using *in vivo* animal models with a view to be demonstrating *in vivo* micro-extraction fibre as a tool for less invasive method for the whole blood metabolomics studies.

Development of Silicon-substituted Fluorophores and their Application to Fluorescence Probes

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Fluorescence imaging is one of the most powerful techniques for visualizing temporal and spatial changes of biological phenomena in living cells, and many fluorescence probes have contributed greatly to biological researches. In particular, xanthene dyes such as fluorescein and rhodamines have favorable characteristics, such as high water solubility and high fluorescence quantum yield, and they have been utilized as fluorescent cores for fluorescence probes working in the green to red wavelength region. Recently, silicon-substituted xanthene dye, 2,7-*N,N,N',N'*-tetramethyl-9-dimethyl-10-hydro-9-silaanthracene (TMDHS)1), has been reported, and we have also designed and synthesized Si-rhodamines2,3) and TokyoMagentas (TMs)4), in which the O atom at the 10-position of xanthene is replaced with a Si atom, as far-red to near-infrared (NIR) fluorescent cores5-8). Fluorescence probes in this color region are highly useful for multicolor imaging with GFP9,10) and *in vivo* imaging11). We expected that fluorescence probes (including dark quenchers12)) based on them would open up new possibilities for imaging biological processes in living biosamples13).

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Developments in the radiochemical analysis of Ac-227 and Pa-231

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Methods for low-level analysis of actinium series radionuclides Ac-227 and Pa-231 have problems with reliability and often employ highly dangerous substances for radiochemical separation, including hydrofluoric acid. This presentation will provide an update on PhD work being undertaken in the development of safer and more reliable radioanalytical methods for these two isotopes. We have developed a new method for the preparation of a Pa-233 tracer using TEVA chromatographic resin which can achieve chemical recoveries over 95% and modified a method for lanthanide hydroxide micro-precipitation to allow alpha spectrometric measurement of Ac-227. Both of these methods will be shown to eliminate the need for the use of hydrofluoric acid and prove simpler alternatives to established procedures.

Direct Interrogating a Key Intermediate in Combustion and Tropospheric Autoxidation

Osborn, D. L.,[1] Savee, J. D.,[1] Papajak, E.,[1] Rotavera, B.,[1] Huang, H.,[1] Eskola, A. J.,[1]
Welz, O.,[1] Sheps, L.,[1] Taatjes, C. A.,[1] Zador, J.[1]

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ABSTRACT TEXT

Oxidation of organic molecules in combustion and Earth's troposphere is controlled by the addition of molecular oxygen to organic free radicals. Among the most important but elusive reactive intermediates during oxidation are hydroperoxyalkyl radicals, often denoted "QOOH." These intermediates are much more reactive than their peroxy-radical isomers (ROO). Because they are carbon-centered radicals, QOOH species can react with an additional O_2 molecule. In combustion chemistry, QOOH is the "switchyard" of oxidation, controlling whether the chemistry is chain inhibiting, propagating, or branching. In the troposphere, the QOOH reactive pathway enables the incorporation of two (or more) O_2 molecules into a volatile organic hydrocarbon, forming low-volatility, highly oxygenated organic aerosol precursors. Using multiplexed photoionization mass spectrometry, we report for the first time direct observation, kinetics, and spectroscopy of a QOOH intermediate in the oxidation of 1,3-cycloheptadiene. The QOOH radical created is highly resonance stabilized, a characteristic that dramatically affects QOOH reactivity. These results demonstrate that oxidation of unsaturated organic molecules, which are ubiquitous in the troposphere, can produced exceptionally long-lived QOOH intermediates.

Discovering New Organic Chemistry Using an Inorganic Touch

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ABSTRACT TEXT

The use of ligands to stabilize compounds containing inorganic species in unusual oxidation states or bonding environments is long-established and widely used. Much less common, and more recently discovered, is the use of ligands to stabilize carbon centred fragments in unusual environments. Most widely known is Bertrand's use of N-heterocyclic carbene (NHC) ligands to stabilize a C_1 fragment in the form of NHC-C-NHC, a highly unusual compound bearing two lone pairs of electrons about the carbon centre. The Dutton group has been using NHC ligands to stabilize C_2 containing fragments. In this presentation we will discuss our synthesis of a complex that can be considered as NHC stabilized acetylene (NHC-CH-CH-NHC), as well as the first example of a diorganoalkene in which the cis configuration is more stable than the trans.

DISSIPATION AND THE PROPERTIES OF NONEQUILIBRIUM SYSTEMS

Bernardi, Stefano[1], Reid, James C.,[1] Rogers, Jarrod[1,2], Evans, Denis J.[3] , Williams, Stephen R. and ***Searles, Debra J.*** [1,2]

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Free energy and entropy are important thermodynamic properties that can be used to understand many physical and chemical changes. However, when a system is far from equilibrium, the definition of these properties becomes problematic. We will discuss the role that dissipation plays in these systems and present an alternative treatment of both equilibrium and nonequilibrium systems based on dissipation. [1]

Some fundamental relationships such as the fluctuation theorems and the dissipation theorem will be presented and we will describe how these can be used to determine system properties. In particular, we will consider the example systems undergoing shear flow.

When a complex fluid undergoes shear flow at high strain rates, the viscosity of the system will change, as will the geometry of the molecules and the structure of the fluid. How this can be quantified using the dissipation theorem, and how this behaviour changes with system size will be discussed. [2]

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[2] Stefano Bernardi, Sarah J. Brookes and Debra J. Searles, "System size effects on calculation of the viscosity of extended molecules", Chemical Engineering Science, **212**, 236-244 (2015).

Dissolution of femtoliter surface droplet arrays in an extensional flow

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ABSTRACT

The dissolution of liquid microdroplets is a critical step in many industrial processes, such as separation and dispersion in food industry and drug delivery and quality control in pharmaceutical industry. To data, there is little exploration regarding the dissolution of micro/nano droplets under extensional flow. Here we show that applying extensional flow accelerates the dissolution process of droplets. The dissolution of microdroplets is faster under faster extensional flow. The individual droplet dissolution behavior is also associated with its location in a droplet-array. A droplet at edge of the array dissolves faster than that at centre of the array. The droplets close to the front of extensional flow commence to shrink earlier than those droplets at the back of the array. Additionally, the droplets move towards the direction of slow extensional flow. The findings suggest potential approaches to manipulation of nanodroplet size in the arrays simply by dissolution. The obtained droplets may serve as microreactors for high throughput analysis or templates for unconventional surface microstructures.

Designed Multiple Ligands Targeting the Dopamine D_2, Serotonin 5-HT_{2A}, and Muscarinic M_1 Receptors

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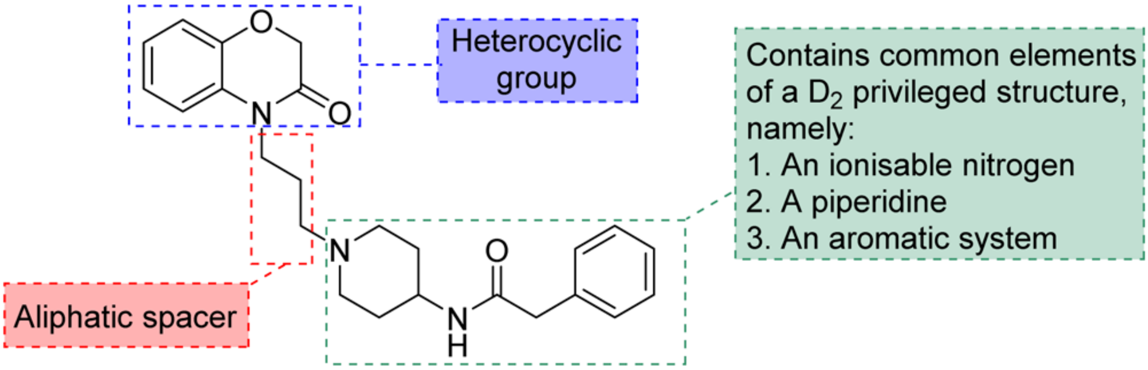
Schizophrenia is a severe mental illness that results in a person being unable to express rational ideas/thoughts or to experience normal emotions, thereby making it difficult to maintain a normal life and healthy relationships (Andreasen2000). There is no single symptom that characterises schizophrenia, but rather a complex set of interrelated symptoms. As such finding drugs to effectively treat all aspects of the disease state is a challenging task. Through our work, we adopted a designed multiple ligand (DML) approach which involves incorporating two separate pharmacophores and slowly increasing the integration between the two until the ligand progresses from a conjugate to a merged structure (Morphy2009). We commenced with a benzoxazinone muscarinic M_1 receptor agonist and merged it with dopamine D_2 receptor privileged structures derived from clinically relevant antipsychotics (Figure 1). We were able to produce a compound that displayed activity at target M_1 and D_2 receptors, in addition to displaying high affinity for the serotonin 5-HT_{2A} receptor, also proven to be useful for antipsychotic efficacy.



Lu AE51090 (**6**)

Figure 1. LuAE51090 and its key features for the development of a merged DML.

DNA based nanocarriers for drug delivery and gene silencing

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ABSTRACT

DNA nanotechnology concept uses the DNA hybridization to build novel structures for use in a wide range applications. One of the research directions in our research group to use the DNA nanotechnology concept to build nanocarrier for drug delivery and gene silencing applications. In this presentation, the construction, characterization and the use of self-assembled DNA tile nanostructures for delivery of chemotherapy drug, doxorubicin, and antisense morpholino oligonucleotides, which designed for the silencing of breast cancer proliferation related genes, will be discussed. DNA tiles were constructed to contain the sticky ends at each arm, which allow for further modifications. To enhance cellular uptake of the DNA tile, sugar molecules and gold nanoparticles (AuNPs) incorporated into the structure through the sticky ends. For drug delivery studies, doxorubicin loaded carbohydrate modified DNA tiles were used and enhanced drug internalization was obtained at various types of cancer cells. Gene silencing studies were carried out using morpholino antisense oligonucleotides, which are nuclease resistant and neutral gene silencing molecules with high target specificity. Morpholinos were embedded into a tile shaped DNA origami structure for knockdown of target genes. The nanostructures were modified with AuNPs for increased cellular internalization. The morpholino embedded DNA tile-AuNPs nanostructures were utilized to deliver morpholinos into breast cancer cells for silencing of HER2, ERα, Ki-67, and EGFR genes. Compared to a commercial liposome based carrier, DNA tile-AuNPs carriers showed more effective silencing of the genes and inhibition of breast cancer cell proliferation was observed after silencing of the targeted genes. The financial support of The Scientific and Technological Research Council of Turkey (TUBITAK) (Project numbers: 112T208 and 115Z426) is greatly acknowledged.

DNA Origami barrels: molecular pegboards assembled from DNA

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ABSTRACT TEXT

Deoxyribonucleic acid, or DNA, is the molecule that encodes the genetic information in all known living organisms. To physical scientists and engineers, it also has huge potential as a programmable building material for biocompatible nanostructures, which can be self-assembled from the bottom up to trillions of copies per milliliter of solution. The most prevalent paradigm for exploring greater complexity has been DNA origami, where a long scaffold strand traverses most or all of the entire shape. We have designed a set of DNA origami barrel architectures, built as stacked rings of double helices, that are robust and modular. These nanostructures are a versatile nanoscale pegboard for applications requiring complex 3D arrangements of matter, with as many as 2000 uniquely addressable pixels spaced 9 nm apart. The DNA barrels are now being used for a range of diverse applications, including tools for biophysics, platforms for diagnostics and therapeutics, and templates for nanofabrication.

SKILLS? WHAT SKILLS? DO SCIENCE UNDERGRADUATES STUDYING CHEMISTRY RECOGNISE OR VALUE SKILLS DEVELOPMENT?

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Employers of Science graduates are seeking a range of transferable skills from job candidates, in addition to discipline knowledge and skills; and academics are increasingly seeking to build employability skill development opportunities into the undergraduate science curriculum. But are students recognising they are developing transferable skills at university and do they understand their importance?

In the highly competitive employment environment currently experienced by Science graduates, it is essential they not only develop the transferable skills sought by employers, but that they recognise they have these skills and that they are valuable. Only then can students articulate these skills to potential employers who are seeking evidence of them during the recruitment process.

Past studies suggest undergraduates may not recognise such skill development without prompting. This presentation will summarise the results of a study of almost 1000 Science students studying Chemistry at two institutions (Monash and Warwick Universities), on the extent to which they recognise course-related skills development and their importance, without being prompted. In addition, the study will address whether student views are consistent across degree types or whether some courses or a particular institution are enabling deeper links with employability skills. Any progress in skills recognition through university year levels will also be investigated.

The results will be discussed in terms of implications for when and how employability skills are introduced, taught and communicated in the higher education Chemistry and Science curricula.

Do We Understand How Molecules Change Their Configuration?

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ABSTRACT

Molecules change their configuration by internal rotation about single bonds. One of the simplest examples involves rotation of a methyl group by 60° to take it from a staggered to an eclipsed configuration.

The understanding of internal rotation is based on the fundamental assumption that this motion is independent of the remaining molecular vibrations. Spectroscopic analyses are performed using computer codes based on this assumption to reveal insights into the molecule and its behaviour, ranging from its geometry (via the rotational constants) to the shape and magnitude of the barriers for internal rotation. In the case of methyl rotation, for example, the toluene rotational spectrum has recently been fit for several torsional (internal rotation) states with a precision of *ca*. 1 part in 10^8, which provides convincing evidence for the validity of the underlying assumption.

In spite of the impressive accuracy with which present computer codes can fit experimental data, we have experimental evidence that this fundamental assumption is not applicable in toluene and have successfully explained its methyl rotation using a model that incorporates interaction between the methyl internal rotation (torsion) and an out-of-plane methyl wag vibration. This torsion-vibration interaction model produces a different set of molecular constants and inferred behaviour than the previous analyses based on torsion and vibration being separate.

The key issue is whether this situation is unique to toluene or relevant to many, or possibly most, molecules. In this presentation the torsion-vibration interaction will be explored in toluene and substituted toluenes.

DOSE-ON-DEMAND PRODUCTION OF DIVERSE ^{18}F-RADIOTRACERS FOR PRECLINICAL APPLICATIONS USING MICROFLUIDICS

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ABSTRACT TEXT

The production of ^{18}F-radiotracers using continuous flow microfluidics is currently under utilised due to perceived limitations in equipment. Additionally, microfluidic technology presents a significant change in methodology compared to the automated radiosynthesis modules currently used in ^{18}F-radiochemistry. We demonstrate the dose-on-demand principle, whereby the back-to-back production of multiple, diverse ^{18}F-radiotracers can be prepared on the same day, on the same microfluidic system using the same batch of [^{18}F]fluoride, the same microreactor, the same high-performance liquid chromatography (HPLC) column and solid-phase extraction (SPE) cartridge to obtain a useful production yield.

Three preclinically relevant compounds were radiolabelled with [^{18}F]fluoride using the Advion NanoTek Microfluidic Synthesis System. The outlet of the microreactor was connected to an automated HPLC injector and following the collection of the product, SPE reformulation produced the ^{18}F-radiotracer in <10% ethanolic saline. A thorough automated cleaning procedure was implemented to ensure no radioactive or UV cross-contamination was observed between radiotracer synthesis. This was confirmed by the >97% radiochemical purity for all the ^{18}F-radiotracers produced. While these three ^{18}F-radiotracers could be produced in yields sufficient for preclinical studies and displayed molar activities >100 GBq/μmol, we will also present some of the challenges that need to be addressed to optimise the dose-on-demand process.

Double-hybrid density functionals: is there anything new to tell?

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Over the past years, we have seen tremendous improvements in the development of quantum-chemical procedures and we now have access to methods that allow the accurate treatment of systems with even hundreds of atoms. However, the large number of available methods also makes it hard for the computational-chemistry user to understand their benefits or potential risks. As a consequence, one can therefore observe the trend to stick to a few familiar — albeit sometimes older — levels of theory, such as the B3LYP or M06-2X density functional theory (DFT) approximations. Meanwhile, the DFT-developer community has acknowledged so-called double-hybrid density functionals (DHDFs) as established methods for treating electronic ground-state properties. Combined with London-dispersion corrections, DHDFs can even be considered as the currently most accurate DFT approximations for (main-group) thermochemistry, kinetics, noncovalent interactions, geometries, and frequencies [1].
In this talk, I will first give a brief overview of the current state of double-hybrid DFT for electronic ground states, before I will discuss recent studies that explored strategies to further modify the current approximations [2,3].

Most researchers in the DFT community are probably unfamiliar with earlier work that has shown DHDFs to be accurate candidates for the calculation of excitation energies [1]. In the second part of my talk, I will therefore review these previous findings, before I will outline our recent efforts to expand relatively recent ground-state DHDFs within the time-dependent DFT framework [4].

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[3] Najibi, A.; Goerigk, L. *manuscript in preparation for J. Comput. Chem.*
[4] Schwabe, T.; Goerigk, L. *manuscript in preparation for J. Chem. Theory Comput.*

Driving Polymer and Surface Modification Using Visible Light

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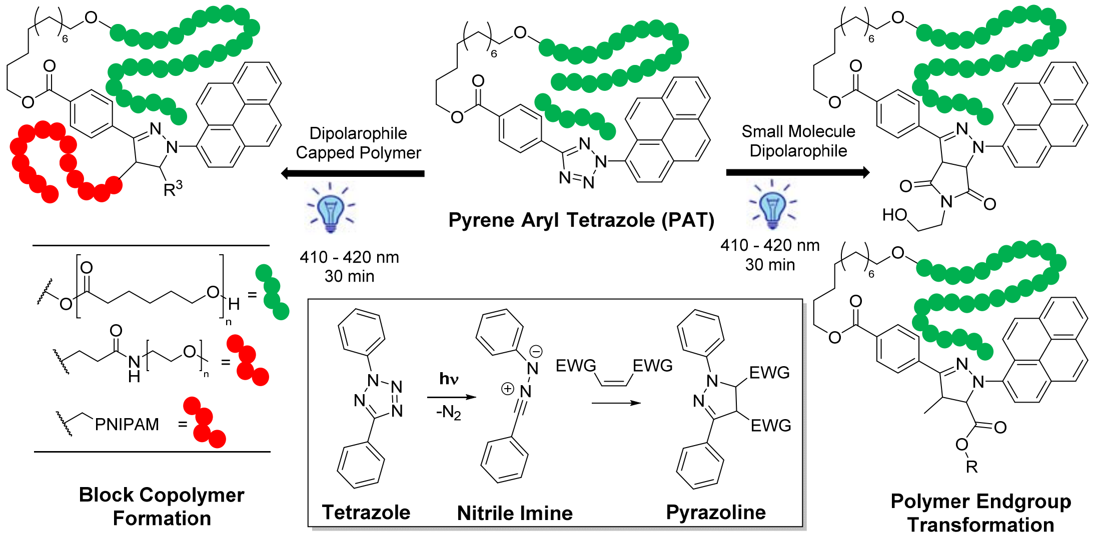
ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

Rapid and catalyst-free cycloaddition systems for visible-light-induced modification of polymers and surfaces will be reported. Photo-reactive azirine and tetrazole moieties were designed to absorb light at wavelengths longer than 400 nm through incorporation of polyaromatic chromophores.[1,2] Irradiation with low-energy light sources enabled quantitative ligation of the photoactivatable unit with functional polymeric substrates achieving full conversion with irradiation times as short as 1 min at ambient conditions. Utilising Upconversion Nanoparticles (UCNP), it was possible to extend the photochemical trigger wavelength well into the NIR regime (980nm).[3] The opportunity for one-pot, UV/Visible wavelength orthogonal photoreactions will also be discussed.[4]



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4. P. Lederhose, A. Welle, D. Abt, R. Mueller, C. Barner-Kowollik, J.P. Blinco *J. Am. Chem. Soc.*, **2017**, *Submitted*

Effect of Chlorine on the Properties of $MAPbI_3$ Perovskite Film

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

Perovskite solar cells (PSC) based on organic-inorganic lead halides material are hailed one of the most promising photovoltaic technologies that can deliver cost-effective solar electricity in the future. Preparation of high quality perovskite film with controlled optical and electronic properties as well as desirable morphology is critical to achieving high energy conversion with the solar cells. It has been reported that perovskite films consisting of mixture of halides such as iodide and chloride perform better in PSCs than the material based on single halide. This phenomenon is attributed to the improved morphology of the perovskite film and reduced recombination in the solar cell devices, leading to longer lifetime of charge carrier and diffusion length. Recently, we have found that introduction of a small amount of chloride (less than 5%) can dramatically modify the electronic properties of the film although it has trivial effect on the film morphology. In particularly, the Fermi-level of the methyl ammonium lead iodide (MAPbI3) film is shifted negatively by 90 meV, leading to an energy level which is more favourable for charge transport at the interface between the perovskite film and adjacent electron transport layer such as TiO_2. As a consequence, the conversion efficiency of the solar cells was enhanced from 16.5% to 19% under one sun illumination (AM1.5 solar spectrum). Further study of the kinetics of electron transfer shows the electron lifetime of the device is enhanced by two-fold through addition of 2.5% (atomic ratio) of chloride in the perovskite film.

Effects Of Temperature On Soil Water Repellence: MD And Experiment

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ABSTRACT TEXT

Hydrophobic soils have been observed around the world, under different climates and land uses[1]. Southern Australia alone has between two and five million hectares affected by hydrophobic soils[2]. These non-wettable soils cause both environmental and economic problems including increased surface runoff, enhanced erosion rates, chemical leaching and reduced crop yields.[3] This hydrophobicity is caused by amphiphilic organic compounds deposited in the soil that originate from plant materials.[4]

Vegetation fire events have been shown to have implications for the dynamics of soil water repellency (SWR). Therefore, this study uses a combination of experimental and theoretical techniques to investigate the effects of temperature on soil water repellency.

The potential of a range of compounds to induce SWR was investigated by applying different loadings on acid washed sand (AWS) and then assessing water repellency as measured with the MED test. Temperature effects were investigated by drying the samples under different conditions. The mobility of compounds found in interstitial organic matter was also investigated by adding this material to AWS and applying different heating profiles.

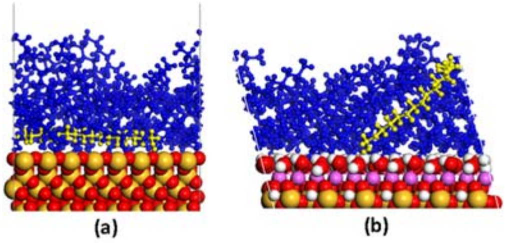

Figure 1. Alignment of $CH_3(CH_2)_{15}OH$ on (a) Quartz and (b) Kaolinite

Experimental measurements were complemented by fully atomistic molecular dynamics simulations and these suggested that poor expression of water repellency by some compounds could be explained by weaker interactions towards the soil surface due to strong molecule-molecule forces.[5,6] Whereas for the long chain hydrophobic molecules the balance between molecule-molecule and molecule-surface interactions favoured surface adhesion, which in turn leads to formation of a hydrophobic layer (Fig. 1). Higher temperatures accelerate the formation of a semi-ordered hydrophobic layer.

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6. S. M. Mijan Uddin, Nicholas R. R. Daniel, Richard J. Harper, David J. Henry, Biogeochemistry (submitted)

Aspects of electrochemical deposition of reactive and inert metals when using ionic liquid electrolytes

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[3] *Towers Group, Surrey Hills North, Victoria, Australia*
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ABSTRACT

Electrodeposition of metals and materials from ionic liquids is attractive due to solvation changes, reactivity and different and/or wider electrochemical when compared to traditional volatile organic solvent or aqueous media. In particular reactive metals such as lithium can be facilely electrodeposited from IL media without the typically associated morphological issues such as dendrite formation. Whilst this is beneficial to devices such as batteries, there are still numerous questions raised about the fundamental deposition mechanism and why the reaction proceeds differently in ionic liquids compared to volatile organic solvents.

We here present an comparative study of electrodeposition of a reactive metal, namely lithium, and a non-reactive metal, silver. By using a multidisciplinary technique we probe the fundamental deposition mechanism from ionic liquids and compare to volatile organic solvent and aqueous media. In doing so we discuss the effect of solvent type on nucleation and growth mechanism, electrochemistry response (e.g. voltammetry and chronoamperometry), deposition morphology, and effects of ionic strength and viscosity. Finally we will discuss the differences in electrodeposition and growth mechanisms for the various solvent types.

ELECTROCHEMICAL INVESTIGATION OF POLYELECTROLYTES AT A LIQUID-ORGANOGEL MICROINTERFACE ARRAY

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ABSTRACT

Polyelectrolytes, defined as polymeric chains that possess a net charge, have been the interest of many studies and applications in several fields, such as biotechnology, pharmaceutical and food industries [1]. Most of their applications are associated with their capacity to electrostatically interact with oppositely charged species and/or surfaces [2]. Thus, investigating the behavior of polyelectrolytes and their interaction with oppositely charged molecules of different nature is a vital component for applications such as sensing. Smaller versions of anionic polyelectrolytes, like sulfated carbohydrates, are vital pharmaceutical agents and can serve as a model for larger sulfated carbohydrates like heparin. In addition, the study on aptamers, larger polyelectrolytes, has been growing due to the many applications it can improve, like protein detection signal amplification [3]. Consequently, simple, and direct methods for the detection of sulfated carbohydrates and aptamers are desirable. As such, the electrochemical characteristics of these polyelectrolytes were assessed using electrochemistry of the interface between two immiscible electrolyte solutions (ITIES), an emerging viable detection technique for biomolecules [4]. This electrochemical approach offers the advantage of label-free detection of ionizable analytes which do not possess redox-activity.

Voltammetry and adsorption/desorption methods were utilized to study sulfated carbohydrates and aptamers under different conditions, revealing that the organic phase electrolyte cation was crucial to generation of a detection signal. Also, the presence of a surfactant was important for aptamer recognition at the interface.
The latest results on polyelectrolyte characterization and detection at the µITIES array will be presented and discussed.

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Electrochemical and Physical Properties of Prussian Blue (PB) composites: stable electrocatalytic materials.

Baiyu Ren, **Lathe A. Jones**,* Daniel K. Oppedisano, Ahmad Kandjani, Miao Chen, Frank Antolasic, Samuel Ippolito and Suresh K. Bhargava

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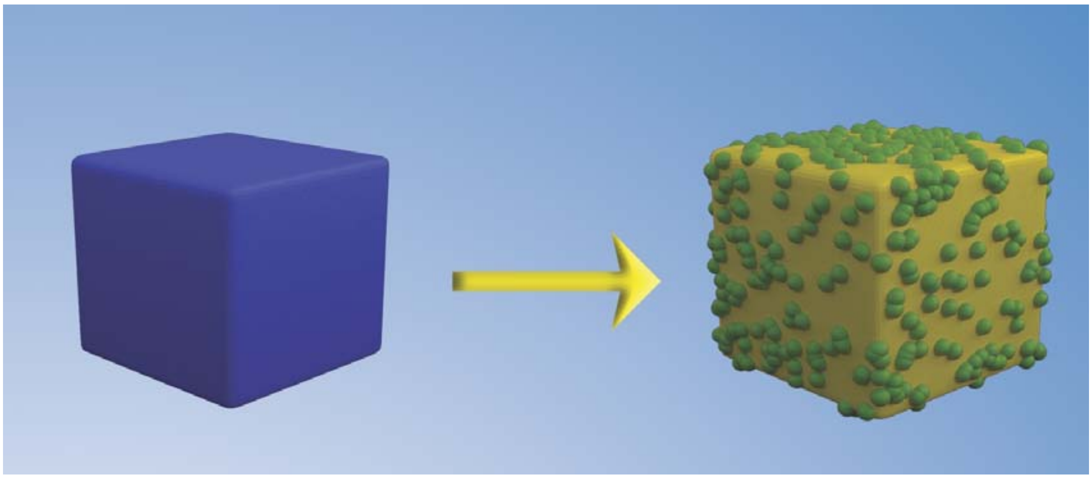
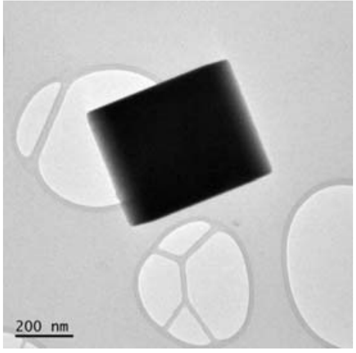
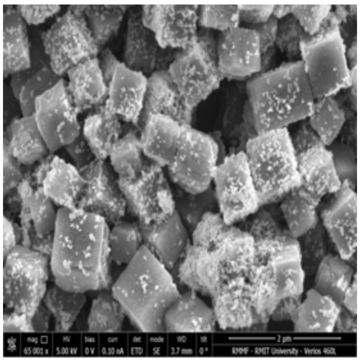
lathe.jones@rmit.edu.au

Galvanic replacement of Prussian Blue cubes with $HAuCl_4$ leads to a stable AuCN/Prussian Blue (PB) Nanocube composite. The composite has an increased surface area and pore volume, but smaller surface pore sizes than pure PB cubes. For electrocatalysis and sensing, the AuCN/PB composite has much improved stability, leading to improved limit of detection and sensitivity for H_2O_2 sensing. This stability was attributed to the stabilization of the surface of PB with AuCN, which prevents decomposition of the reduced $Fe^{II}Fe^{II}$ derivative of PB during electrocatalysis. The new material shows that redox active Molecular Organic Frameworks (MOFs) used for electrochemical sensing or catalysis can be tuned for surface porosity, and stabilised via galvanic replacement with a noble metal salt, leading to improved electroanalytical performance. A range of similar materials under development will also be discussed.





Schematic of composite synthesis (above), and images of PB (left) and PB composite (right)



Electrochemiluminescence Resonance Energy Transfer system: Application in Immunosensor for β-amyloid

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ABSTRACT TEXT

Electrochemiluminescent (ECL) assay has gradually drawn increasing interest to be considered as one of the potential strategies to be applicable in a wide range of target determination. This paper proposed a new methodology for ultrasensitive and facile detection of Alzheimer's disease marker β-amyloid by fabricating a sandwich-type electrochemiluminescence sensing platform. Herein, resonance energy transfer(RET) of electrochemiluminescence was employed to determine β-amyloid concentration, which can be attributed to the quenching effect between $Ru(bpy)_3^{2+}$ and gold nanorod acting as ECL-RET electron donor and acceptor, respectively. In this protocol, mesoporous carbon nanospheres was adopted as the substrate material to immobilize ECL reactant $Ru(bpy)_3^{2+}$ and antibody via nafion to acquire the RET donor nanocomposite (MOCs/nafion/ $Ru(bpy)_3^{2+}$/Antibody). It is of vital importance that gold nanorod with exquisite rod shape was synthesized and exhibited a typical absorption peak at 610nm to quench ECL signal of $Ru(bpy)_3^{2+}$ effectively. Moreover, the RET acceptor nanocomposite (GNRs/Aptamer) was composed of gold nanorod and thiol functionalized aptamer via Au-S bond. The influences of TPA concentration, incubation time between antibody and antigen and incubation time between antigen and aptamer were indeed investigated. Under the optimal conditions, the intensity of the ECL immunosensor decreased linearly with the logarithm of β-amyloid concentration in a wide linear range from 1.0×10^{-5} to 100 ng/mL with a detection limit of 3.33×10^{-6} ng/mL (S/N=3). Furthermore, high sensitivity, booming stability and reproductivity were verified to declare the promise for being applicable to analyze the β-amyloid content in real Alzheimer's cerebrospinal fluid samples with satisfactory results.

Elegant surface of CoNi alloys toward efficient magnetorheological performances

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ABSTRACT

Magnetorheological (MR) fluid is a kind of smart materials whose rheological behaviours can be tuned by the external magnetic field. It consists of micrometer-sized magnetizable materials dispersed in a liquid carrier. When an external magnetic field is applied, particles of the MR suspension get polarized and develop magnetic moments, resulting in the formation of chain-like structures aligned with the applied field. These field-induced structures hinder the free flow of the former Newtonian fluid, enhanced yield stress and viscosity are observed. The magnetic controlled intelligent fluids have already been utilized in semi-active devices such as shock absorbers, torque transducers, clutches, brakes, tunable dampers and clutches. The surface roughness and wettability between oil and particles are critical factors affecting their MR effects. In contrast to conventional carbonyl iron (CI) particles, transition metals cobalt (Co), nickel (Ni) and their bimetallic alloys provide a viable alternative attributed to their high saturation magnetizations, and well control of morphology. In this study, CoNi alloys are introduced using a simple hydrothermal process. Carbon quantum dots (CQDs) were adopted as surfactants for adjusting the surface roughness and affinity of the CoNi alloys, as shown in Figure 1. The obtained CoNi alloys with elegant surface revealed better magnetorheological properties compared to the pristine CoNi alloys.

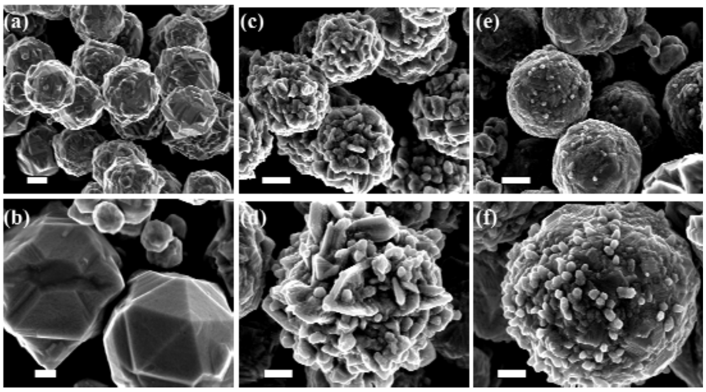

Figure 1 SEM images of pure CoNi alloys (a, b), CoNi alloys with CQDs at concentration of 0.025mg/ml (c, d) and 0.05ml/ml (e, f). The scale bars in the first row are 400 nm, in the second row are 200 nm.

Analysis of Metals (toxic & essential) in Foods and Assessment of Intakes in Selected Children

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ABSTRACT

An increased exposure to toxic metals such as arsenic (As), cadmium (Cd) and lead (Pb) either through diet, water and air in the young children has caused concern to many countries. Deficiency of essential trace elements such as iodine (I) and selenium (Se) is also a major concern in young children which can affect their mental development and growth. In this study, the duplicate diets of selected healthy children (n=15) were collected over 3 consecutive days. Other selected food items were obtained from food market outlets in Brisbane, Australia. The elemental levels in the diets and food items were analysed by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion. Appropriate standard reference materials were used for quality control and method validation. The study showed wide variations of daily intakes of these elements in these children. The intakes ranged from 36.9 to 288 µg/day (93.1 ± 76.7 µg/day) for I; 16.1 to 66.0 µg/day (45.6 ± 17.6 µg/day) for Se; 1.7 to 31.2 µg/day (11.5 ± 8.9 µg/day) for As; 0.98 to 9.5 (4.0 ± 2.2 µg/day) for Cd; and 0.90 to 11.7 (5.6 ± 3.5 µg/day) for Pb. The daily intakes of these trace elements in these children were comparable with reported values in children of other countries.

Emergent Magnetism From Lithium Freezing in Lithium Doped Boron Nitride

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

The synthesis and characterisation of Li doped boron nitride is reported where the sample is in the dilute limit with a stoichiometry of Li0.01 (BN)3 . It appears that the Li diffusion dominates above 150 K, with DLi ~ 10−10 cm2 s−1 , where the Li diffusion rate increases with temperature resulting in activated behaviour with an energy scale of 27 meV. Below 150 K the Li diffusion freezes out and the sample enters a magnetic state at approximately 70 K that shows evidence for being glassy in nature. It is believed that this is due to the freezing of Li atoms within the lattice which then involves partial electron injection into the BN layers, and this provides a mechanism for magnetic exchange, resulting in a divergence of the magnetic susceptibility. Our work shows the promise of this material for future study, where there is currently much interest in Li base compounds for energy storage.

EMERGING CONTAMINANTS IN MARINE ENVIRONMENT OF THE BAY OF BENGAL

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The Bay of Bengal is located at the northeastern end of the Indian Ocean and has an area of 2,172,000 km². Several major rivers run into the Bay of Bengal. The coastal areas of Bangladesh (along the Bay of Bengal) include 60% of the Sundarbans, the mangrove forest of the Ganges/Brahmaputra delta in the west and areas with coral reefs in the Cox's Bazar provinces in the east. These areas are economically important because of fishing and biodiversity due to rich source of flora and fauna. Recently, marine plastic debris and microplastics have risen as one of the most important environmental issues globally. Several studies have covered the situation in the Pacific and Atlantic Oceans, but very little is known about the situation in Bay of Bengal. We are studying emerging contamination including microplastics, phthalates, organochlorine compounds, PAHs, heavy metals etc. on the sensitive ecosystems of the Sundarbans, and 20 marine fish, 30 water and 15 soil samples were collected from the area to investigate possible occurrence. Gastrointestinal tracts of fish species were digested in 10M NaOH at 60 ºC for 24 hours followed by filtration on Millipore membranes (0.45 µm) and finally dried materials were analyzed by FT-IR. Organochlorine compounds (DDTs and PCBs) and heavy metals (Cd, Cr, Hg and Pb) and arsenic were analyzed by *gas chromatography coupled with electron captured detector (GC-ECD) and atomic absorption spectroscopy (AAS), respectively. Low amount of the environmental contaminants were found in these samples.*

Energetics of akamptisomerisation: the last fundamental type of conformational isomerism

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Chemical reaction pathways pertaining to the final fundamental form of conformational isomerization to be discovered are characterized. This form of isomerization, identified as previously unobserved through extension of the polytope formalism, involves bond-angle inversion and is demonstrated through synthesis and characterisation of four resolved stereoisomers of a transoid (BF)O(BF) quinoxalinoporphyrin. These comprise two pairs of enantiomers, manifesting structural relationships not describable within existing IUPAC nomenclature and terminology. We propose the term "akamptisomerisation" to describe observed thermal diastereomeric interconversion processes occurring over a bond-angle inversion barrier of 104 ± 2 kJ mol^{-1}. The general process of strepsisomerisation in macrocyclic ligands is also introduced and characterised computationally, with two sets of sequential akamptisomerisation and racemisation steps transforming all products into each other in a cyclic fashion. We also introduce the new stereodescriptors parvo and amplo to describe the two coordinated atoms (here borons) with respect to their non-local environment (here a low-symmetry porphyrin). Density-functional theory calculations map out interconversion processes between conceivable synthesis products and reaction intermediates, with all 37 considered species successfully named using our new notation. Many classes of compounds and polymers could involve akamptisomerisomers.

Engineering Nanocellulose Gels for Biomedical Applications

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ABSTRACT TEXT

Hydrogels are fascinating soft materials consisting of polymeric networks which entrap substantial amounts of water (~99wt. %). Cellulose, the most abundant polymer occurring in nature, can be processed into nanofibers and biodegradable, biocompatible hydrogels. Carboxylated nanocellulose fibres which form hydrogels present interesting potential for high value products, particularly in food and biomedical applications. However, characterisation and fundamental understanding of their gelation mechanism are required to efficiently engineer their property for specific applications.

Here, TEMPO-oxidised cellulose nanofibres are used to produce hydrogels. A combination of techniques – rheology and dynamic light scattering (DLS) – were employed to characterise the structure and understand the mechanism of hydrogel formation. We have determined that the formation of gels and their properties are heavily influenced by fibre concentration. Moreover, gel colloidal stability is dependent on factors such as pH and ionic strength, affecting swelling and bond strength. The combination of critical length-scale and high surface charge density of the nanocellulose fibres allows the formation of stable colloidal gels.

Through control of this structure-property relationship, we are modifying and functionalising hydrogels by optimising fibre content, their response to environment (ionic strength and pH) and modifying surface composition or complexing with polyelectrolytes. The first part of the talk will present hydrogel properties; the second will develop these nanocellulose gel for blood analysis applications.

Engineering Photocatalytic Nanocellulose Paper: Effect of Structure and Nanoparticle Aggregation.

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Waste waters emitted from industrial plants can contain significant amount of organic pollutants which can migrate into ground water wells and surface waters to harm humans and environment. Titanium dioxide nanoparticles (TiO_2 NPs) present attractive options for the decomposition of environmental pollutants thanks to their effective photocatalytic activity. TiO_2 NPs are low cost semiconductors of high surface area. On their own, TiO_2 NPs are difficult to process as they are challenging to separate and recycle from the reaction medium because of their nano-size. TiO_2 NPs also tend to agglomerate upon spikes in pH and ionic strength, reducing the photocatalytic activity. Embedding TiO_2 NPs into a nanocellulose matrix opens up a new path to tailer high performance photocatalytic active paper. However, there is little information available relating paper composition and structure to photocatalytic activity. Particularly missing the effect of TiO_2 aggregation state and the catalytic performance.

Here, we developed novel flexible nanocellulose-TiO_2 composites with different loadings (10-60 wt%) of TiO_2 NPs, and also different engineered structures of relying on the same TiO_2 NP loading. Control of composite structure and TiO_2 state were achieved by controlling the surface coverage and type of polyelectrolyte added in a two-step process. Small angle X-ray scattering was used to measure the aggregation state. We relate content and aggregation to photocatalytic degradation using methyl orange as a model aromatic organic compound. The first part of the talk will present composites properties and catalytic performances; the second will analyse the finding in the context of industrial water treatment.

Enhanced Electromechanical Properties of Textured $Bi_{0.5}Na_{0.5}TiO_3$-Based Ceramics

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Piezoceramics have applications in sensors, actuators, and energy harvesters etc,. However, these piezoelectric devices are developed from lead-based ceramics because of their better performance. Nevertheless, lead-based ceramics are toxic and face constraints from global legislative agencies. Therefore, numerous research efforts have been employed to synthesize high performance lead-free ceramics for practical applications. In this work, lead-free textured 0.94($Bi_{0.5}Na_{0.5}TiO_3$)-0.06$BaZrO_3$ (BNT-BZ) ceramics were prepared by a reactive templated grain growth (RTGG) method followed by tape casting utilizing BNT templates. The anisometric plate-like BNT templates were synthesized from the $Bi_{4.5}Na_{0.5}T_4O_{15}$ (BNT4) precursors by a topochemical microcrystal conversion (TMC) method. Their crystalline phase, microstructure, dielectric and piezoelectric properties were investigated and compared with non-textured samples of the same composition prepared by a conventional solid state reaction method. Pure perovskite structure without any evidence of secondary phase was observed for both compositions. Structure analysis confirms that textured BNT-BZ ceramics orient along {100} plan and exhibit a grain orientation factor above 80%. Moreover, the piezoelectric properties of textured BNT-BZ ceramics were enhanced as compared with non-textured ceramics. These results show that BNT templates are effective in inducing grain orientation and enhancing the electromechanical properties of the BNT-BZ ceramics.

Enhancement of the Bioactivity of Laccase for Biosensing and Decontamination

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ABSTRACT

Simultaneously enhancing the catalytic bioactivity and stability of enzyme is still an intractable issue in the enzymatic study. Herein, a facile and effective approach was designed to immobilize and modify laccase on a Cu^{2+}-adsorbed pyrene-terminated block copolymer [poly (acrylic acid)/poly (poly (ethylene glycol) acrylate)] (PAA/PPEGA), which was prepared via well-controlled reversible addition-fragmentation chain transfer polymerization. PAA provided the supporting matrix for firm immobilization of Cu^{2+}, an enzyme bioactivity inducer, onto the microstructure of laccase, while avoiding any contamination of the heavy metal Cu^{2+} into the following application system. The water-soluble, biocompatible and nontoxic PPEGA was used as an ideal modifier to improve the laccase stability. Accordingly, the modified laccase exhibited enhanced catalytic bioactivity and stability simultaneously to 447% and 237%, respectively. The modified laccase was immobilized on the highly oriented pyrolytic graphite surface and large-area graphene papers through π−π stacking interactions between the pyrene moiety of PAA/PPEGA and the π-conjugated graphene-like surface. The as-prepared portable solid-state electrochemical laccase biosensor showed lowest detection limit of 50 nM (S/N ≥ 3) and long-term stability for pyrocatechol detection. Besides, the laccase immobilization on graphene paper provided efficient pyrocatechol decontamination platform with convenience and recyclability, which could retain the laccase bioactivity of 176% after 8 consecutive operations.[1]

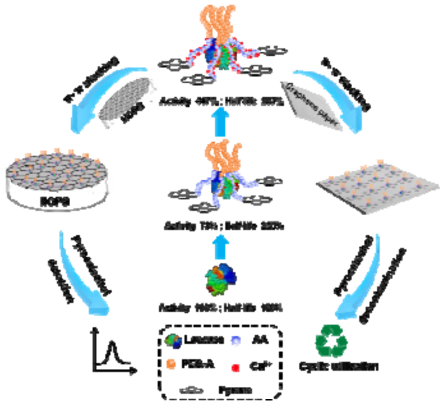

Figure 1 Enhancement of bioactivity and stability of laccase by Cu^{2+}/PAA/PPEGA matrix for efficient biosensing and recyclable decontamination of pyrocatechol.

Enhancing chemical transformations using immobilised catalysis in dynamic thin films under continuous flow

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The catalysis of organic reactions using immobilized palladium nano-particles (Pd NPs), and other metals, within the Vortex Fluidic Device (VFD)[1] will be presented. The VFD is capable of inducing intense shear, high mass transfer and intense micro-mixing under microfluidic, turbulent flowing liquid thin films. Catalysts play an essential role in the synthesis of fine chemicals, active pharmaceutical ingredients (APIs) and intermediates. However, several problems exist such as scale-up and catalyst recovery, and reuse, where such challenges often limit the use of otherwise useful catalysts in industrial scale processing. The attachment of catalysts to the VFD tube and the installation of ultra-thin 'cartridges' for synthesis in continuous flow has the potential to overcome these challenges and enhance organic reactions. An immobilised catalyst in the VFD will be applied to several organic transformations to showcase its effectiveness and versatility. The application of multiple metal catalysts within a single VFD tube for multi-step continuous flow synthesis[2] will also be explored.

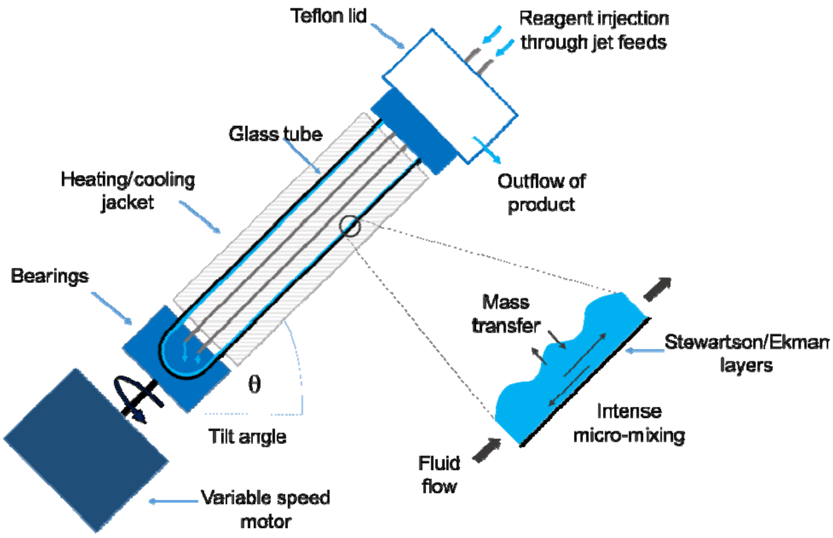

Figure 1: Schematic of the Vortex Fluidic Device (VFD).

(1) L. Yasmin, X. Chen, K. A. Stubbs and C. L. Raston, *Sci. Rep.*, 2013, **3**, 2282

1. J. Britton, J. Chalker and C. L. Raston, *Chem. Eur. J.*, 2015, **21**, 10660 - 10665

EVALUATION OF METHANE EMISSIONS FROM THE AGRICULTURAL SECTOR IN FIJI

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Several studies have been done on methane (CH_4) emissions from the agricultural sector from Asia, the United States and Australia however data from tropical South Pacific is scarce. This presentation looks at the evaluation of CH_4 emissions from the agricultural sector in Fiji particularly from rice cultivation and enteric fermentation. A passive observational study using the static chamber method was done on two rice (*Oryza sativa* L.) varieties (Star and Totoka) to determine the seasonally integrated methane fluxes which were found to be 247.26 mg $m^{-2}day^{-1}$ and 134.27 $gm^{-2}day^{-1}$ for Star and Totoka respectively. Since there were statistically no significant differences (p-value > 0.05) between the means of the flux from the two varieties, an average flux value was used to determine the total CH_4 emitted from the irrigated rice farms in Fiji. This equated to 0.06 Gg $year^{-1}$ for the year 2014. The flux values obtained over the season showed a weak positive correlation with light intensity levels, atmospheric and chamber temperatures for both varieties. The other aspect of this presentation is the estimation of the total annual CH_4 flux from enteric fermentation. These were determined to be 2.64 Gg yr^{-1}, 2.46 Gg yr^{-1}, 0.19 Gg yr^{-1}, 0.08 Gg yr^{-1} and 0.03 Gg yr^{-1} for beef, dairy cows, goat, sheep and pig respectively based on the livestock population in 2014 using the Intergovernmental Panel on Climate Change (IPCC) models and guidelines. On a global scale, methane emissions from enteric fermentation is increasing however in Fiji there is a slow rise compared to other developed and developing countries. The total methane emissions from the agricultural sector in 2014 that includes emissions from enteric fermentation and two rice ecosystems (irrigated and rainfed) was 154179.93 tonnes of CO_2 equivalent. The emission factor determined in this project will validate national greenhouse gas inventory and be instrumental in projecting future emissions from the agricultural sector.

Exciton polaritons in organic molecular crystals

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In this contribution, we present a working theory on exciton polaritons in organic molecular crystals. We calculate the reflection and refraction of light from a surface of oriented Lorentz oscillators for frequencies near the resonance of the oscillators by solving the controversial additional boundary conditions for exciton polaritons using vector potentials rather than fields.

Reflection of light from a uniaxial material results in a spectrum featuring a characteristic minimum in the middle of the reflection band that is in agreement with experiments (see Fig 1a). The minimum in reflection is related to the excitation of polaritons in the crystal. [1] We also predict trirefringence, i.e. the refraction of an unpolarized incident light beam into three separate beams with different polarization, as shown in Fig 1b, that occurs when light is refracted at the internal boundary between a biaxial material and vacuum. This new phenomena emerges from the possibility of longitudinally polarized polaritons in the material next to transversal modes.

The resulting theory provides a comprehensive account of reflection and refraction beyond the traditional Fresnel equations unifying the optics of designer and conventional materials. [2]

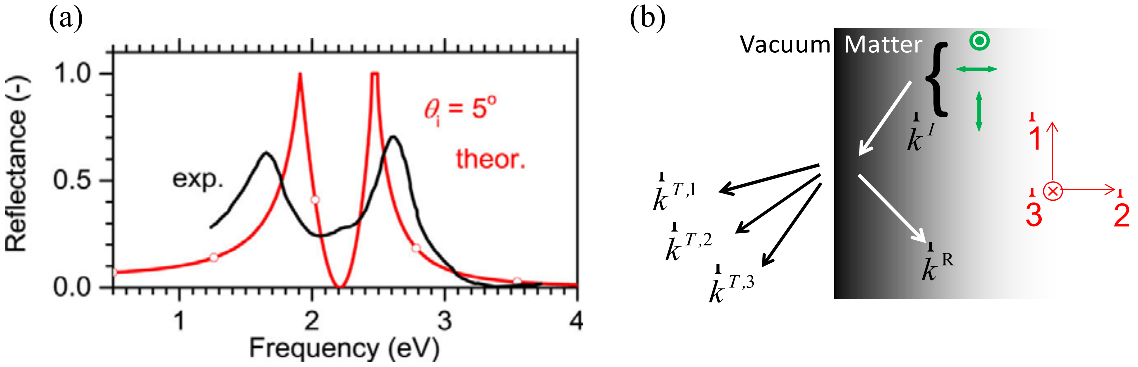

Fig. 1. (a) Experimental reflectance for a crystal of squarylium dye molecules compared to the calculated reflectance spectrum (red line) for reflection from a face of a cubic lattice of Lorentz oscillators predicted for by the dipole oscillator model for near-normal incidence, assuming a cubic lattice. (b) Geometry of incoming and refracted rays and orientation of the laboratory axes, which are assumed to coincide with the principal axes of the polarizability tensor of the material

References

[1] S.C.J. Meskers, G. Lakhwani, *J. Chem. Phys.* 2016, **145**, 194703
[2] S.C.J. Meskers, G. Lakhwani *Arxiv:1601.04014 [cond-mat.mtrl-sci]*, 2016

Expanding the scope of naphthalimide fluorescence

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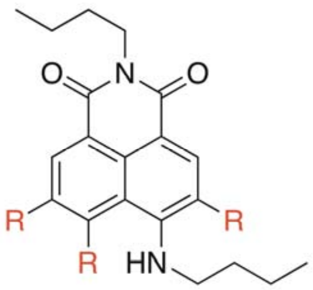
Fluorescence microscopy has become an indispensible technique for studying cellular biology. At the center of this technology lies the fluorescent reporter molecule. There are many classes of fluorophore for which the fluorescence mechanism is well characterised and understood, and this has led to the design of many derivatives with favourable properties for biological imaging. In contrast, 1,8-naphthalimides are a commonly used but under-explored class of fluorophore, with only a few key mono-substituted derivatives reported in the literature, which span a very limited range of photophysical properties.

The synthesis and characterisation of a library of 1,8-naphthalimides bearing various functional groups at three positions on the naphthalimide scaffold, along with the effect of these modifications on the photophysical properties of the molecules will be presented. The synthesised naphthalimides exhibit a much more diverse range of photophysical properties than has previously been seen in this class of fluorophore. These results allow elucidation of some structure-photophysical property relationships for di-substituted naphthalimides.



R = NH_2, H, Br, SO_3H, NO_2

Experimental Evidence For SOMO-HOMO Conversion in Distonic Radical Anions

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ABSTRACT TEXT

For most free radical species, the singly-occupied molecular orbital (SOMO) is also the highest-occupied molecular orbital (HOMO). This is consistent with the Aufbau principle whereby electron pairs are assigned to molecular orbitals in order of increasing energy; leaving the unpaired electron in the orbital of highest energy. For some radical ions, however, molecular orbital calculations predict the SOMO to be lower in energy than the HOMO; a phenomenon known as SOMO-HOMO energy-level conversion (Gryn'ova, Nature Chem. 2013). Calculations on radical anions indicate that this conversion can occur where a sufficiently stable radical is spatially separated from, and not in resonance with, a negatively charged moiety that exhibits higher-energy doubly-occupied orbitals. This intriguing phenomenon is associated with significant stabilisation of the radical, which can be measured as a decrease in the gas-phase acidity of ca. 20 kJ mol^{-1} (0.2 eV) in the conjugate acid. In principle therefore, less energy should be required to remove an electron from a radical anion of this type compared with a closed-shell analogue. To test this hypothesis, negative ion photoelectron spectra were acquired for the distonic radical anions of 4-carboxy-TEMPO and 3-carboxy-PROXYL along with their closed shell methoxyamine analogues. These spectra indicate a shift in the vertical (and adiabatic) electron binding energies of ~0.2 eV in favour of the radical anion. This observation is in good agreement with the computed energy-level separation between the SOMO and HOMO orbitals in the radical anion, and provides the first direct experimental window into their electronic structure.

Experimental Replication of Titan's Cyanide Haze Atmosphere

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Saturn's largest moon Titan, in many ways, resembles the Earth environment. It possesses a dense atmosphere and surface liquids where chemistry is observed to unfold. The two main atmospheric components - CH_4 and N_2 – partake in photochemical reactions to produce small nitrile and hydrocarbon species. These are then further processed to complex organic molecules. For example, polymeric nitriles ('tholins') coagulate into ice-coated aerosols that precipitate from the cold upper atmosphere. It is thought such condensed-phase nitriles are responsible for a prominent far-infrared absorption feature at 220 cm^{-1} that remains unassigned after many years of scrutiny.

In recent years following the Voyager and Cassini-Huygens space probes, there have been a number of experimental analyses on tholins under conditions replicating the Titanian environment. There have been comparatively few laboratory far-IR studies to probe the temperature and pressure dependence on size distributions and morphology of binary-phase particles. Without such an understanding, the fundamental microphysics and optical constants of these aerosols cannot be ascertained; inhibiting features such as the 220 cm^{-1} band from being assigned.

In this talk, we will present the first far-infrared studies of select nitrile aerosols under Titan atmosphere conditions. We use a specialized enclosive-flow-cooling-cell located at the Australian Synchrotron THz/Far-IR beamline - the only setup in the world that can analyse atmospheric aerosols in the far-IR under planetary conditions. Our work will be modelled using a discrete dipole approximation approach developed for binary ices with our spectra compared to recent Cassini-Huygens mission data.

Exploiting Gold Catalysis for Complex Molecule Synthesis

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In this presentation, we will disclose our recent contributions toward developing gold(I)-catalysed methodologies that are practical and of potential use in natural products and functional materials synthesis. The talk will cover the current results of an on-going program focused on realising new and efficient synthetic routes to structural targets of current biological and materials interest from readily accessible 1,*n*-diyne esters. For example, we will present a synthetic method to prepare 2,4a-dihydro-1*H*-fluorenes efficiently from Au(I)-catalysed cycloisomerisation of 1,6-diyne esters. In this work, the suggested reaction pathway provides rare examples of [2,3]-sigmatropic rearrangement reactivity in this class of compounds as well as the involvement of an in situ formed cyclopropene intermediate in gold catalysis.

Exploring glycerol composites as solvents for extraction of plant metabolites

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Glycerol composites prepared with nonhazardous naturally occurring organic compounds have been proposed as 'green' alternatives to organic-based solvents due to the low flammability, toxicity, cost, vapour pressure, and environmental impact of glycerol [1]. This project explores the use of binary glycerol composites in the extraction of plant metabolites from *Calendula officinalis*. Ultrasonic extracts prepared from *C. officinalis* were analysed for metabolite concentration (Ultra High Pressure Liquid Chromatography), phenolic content (Folin-Ciocalteau Assay), and antioxidant activity (Sequential Injection Analysis – Chemiluminescence), and show improved extraction when compared with a typical water and ethanol extract. Metabolite concentration, phenolic content, and antioxidant activity were found to correlate to the dielectric constant and chaotropicity (hydrogen bond disruption capability) of the composite.

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Extracellular Metal-Bridges Regulate Uptake of Fluoroquinolone: A Bacterial Self-Protection Strategy

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Bacterially extracellular biofilms play a critical role in relieving toxicity of fluoroquinolone antibiotic (FQA) pollutants, yet it is unclear whether antibiotic attack may be defused by a bacterial one-two punch strategy associated with metal-reinforced detoxification efficiency. Our findings help to assign functions to specific structural features of biofilms, as they strongly imply a molecularly regulated mechanism by which freely accessed alkali-earth metals in natural waters affect the cellular uptake of FQAs at the water-biofilm interface. Specifically, formation of alkali-earth-metal (Ca^{2+} and Mg^{2+}) bridge between modeling ciprofloxacin and biofilms of *Escherichia coli* regulates the trans-biofilm transport rate of FQAs towards cells (135-nm-thick biofilm). As the addition of Ca^{2+} and Mg^{2+} (0-3.5 mmol/L, CIP: 1.25 μmol/L), the transport rates were reduced to 52.4% and 63.0%, respectively. Computational chemistry analysis further demonstrated a deprotonated carboxyl in the tryptophan residues of biofilms acted as a major bridge site, of which one side is a metal and the other is a metal girder jointly connected to the carboxyl and carbonyl of a FQA. The bacterial growth rate depends on the bridging energy at anchoring site, which underlines the environmental importance of metal bridge formed in biofilm matrices in bacterially antibiotic resistance.

Fabrication of Detection Devices Focus on Fused Deposition Modelling 3Dprinting

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The designs of detection devices and sensors are highly specific depending on the detection type. There is an increasing demand for rapid means of design and fabrication of complex detection devices, as this is often a too challenging task when using traditional fabrication techniques of subtractive manufacturing. 3D printing as a fast growing group of additive manufacturing techniques is becoming increasingly popular as a simple and convenient alternative. The coupling of computer aided designs with 3D printer allows transformation of digital designs in to physical models which not only speeds up the fabrication process but also makes it practically suitable for simple and quick testing of the different designs and hence speeding up the development process dramatically. This allows for the adaptation of a "fail fast, fail often" approach in optimising designs. The material to create a part or prototype is highly dependent on the 3D-printing technology used, with fused deposition modelling (FDM) providing the widest range of materials including PLA (polylactic acid or polylactide), ABS (acrylonitrile butadiene styrene) and specialised materials including glass reinforced polymers and bioresorbable materials. FDM has been previously used for the creation of interfaces and customised parts to facilitate laboratory experiments. The aim of this project is to design and fabricate next generation miniaturized, low cost devices applicable in portable microfluidic systems by using a FDM 3D printer. Multiple materials will be used to allow one-piece fabrication of all parts of detection device including integrated electroosmotic pumps and pneumatic valves. This will provide a simple and inexpensive detection device that will be used for task such as on-site pH monitoring of a wide range of environmental samples at various locations.

FABRICATION OF ULTRASENSITIVE NANOBIOSENSORS BY CO-ENTRAPMENT OF NANOMATERIALS AND ENZYMES

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The fabrication of chemical sensors and biosensors in recent years has been considerably influenced by the increasing presence of wide ranging nanomaterials, such as metallic nanoparticles, graphene and carbon nanotubes. This is due largely to the unique electronic, chemical and physical properties that these nanomaterials possess. Some of the specific advantages these nanomaterials offer for fabrication of sensors include high surface energy, high surface-to-volume ratio, and their abilities to act as electroconducting pathway for accelerating electron communication. Despite these potential benefits, the critical step in successfully using these nanomaterials for fabrication of nanobiosensors relies significantly on their biocompatibilities and the ability to successfully integrate the nanomaterials with the chosen biomolecule(s). While there are a number of established methods for immobilisation of biomolecules, such as enzymes, for fabrication of biosensors, not all of these methods are capable of achieving the direct co-immobilisation of biomolecules and nanomaterials that is required for fabrication of ultrasensitive nanobiosensors.

In this talk, we will present the various approaches developed for the direct co-entrapment of gold nanoparticles, carbon nanotubes and gold nanowires arrays with a range of enzymes for fabrication of ultrasensitive biosensors for sulfite, nitrate, phosphate, cholesterol and penicillin. We will also highlight the benefit of the direct co-entrapment in minimising the required enzyme concentration and, hence, cost. Furthermore, the synergistic effect and benefit of co-entrapment of more than one nanomaterial with the biomolecule will be demonstrated, as well as application to the analysis of real samples

Fiber-shaped Supercapacitors with Ultra-high Energy Density for Wearable Electronics

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Fiber-shaped supercapacitors (FSCs) that have the merits of tiny volume, high flexibility and wearability are attractive as power sources for miniaturized electronic devices, such as micro-robots, wearable electronic textiles and implantable medical devices. However, compared with batteries or traditional capacitors, FSCs show much lower-energy density and suffer from extra challenges in mechanical performance. According to the equation ($E = 0.5CU^2$), energy is proportional to capacitance and potential windows. So it is crucial to explore high capacitance fibers with high operating voltage and good mechanical properties for FSCs.

We present a general and effective approach in developing high performance fiber-shaped supercapacitors based on the conducting polymer for wearable electronics. In our study, we increase the capacitance and energy density of Electric-double layer capacitors (EDLCs) by increasing the fiber interfacial area and the operating voltage. First, we adopt a simple pipe mold method to fabricate hollow RGO/PEDOT-PSS composite fibers with excellent flexibility and conductivity. The symmetric solid-state FSCs composed of two HCFs reveal a high specific areal capacitance of 304.5 mF cm^{-2} at 0.08 mA cm^{-2}, corresponding to an high energy density of 6.8 μWh cm^{-2} at a power density of 16.6 μW cm^{-2}.

Furthermore, PEDOT-PSS fibers with operating voltage of 1.8V will displayed. By increasing the operating voltage up to 1.8V, the energy density of the FSCs show an ultra-high areal energy density of 33.2 μWh cm^{-2} (based on single fiber electrode) or 8.3 μWh cm^{-2} (based on entire devices) with a maximum power density of 1600 or 400 μW cm^{-2}.

In this presentation, we will discuss the fiber formation mechanism, charge storage mechanism and display the flexible wire-shaped energy device constructed by the fiber supercapacitors.

Acknowledgements

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Finding fragments and following them up: lessons learned

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Fragment-based drug design (FBDD) has continued to grow in popularity and impact with the recent approval of the second FBDD derived drug venetoclax.[1] At Monash University the recent initiation of the Monash FBDD Platform (MFP) has allowed for re-examination of the workflow for screening and validation. Here we present our recent learnings from the past 2 years since initiation of MFP. These include approaches to fragment QC, analysis of mixture effects and ranking in NMR mixture screening with respect to validated compounds. In addition we will provide a brief overview on implementation of a new workflow for fragment hit development utilizing the recently reported Off-rate screening (ORS) strategy.[2] In this presentation I will describe our approach to the chemoinformatic design and validation of standardised reactive reagent libraries suitable for parallel micro scale synthesis. This new workflow allows for the Rapid Elaboration of Fragments into Leads (REFiL) that, at its heart, uses ORS on minimally purified compounds.

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Fluorescent Methods for the Detection of Heavy Metals

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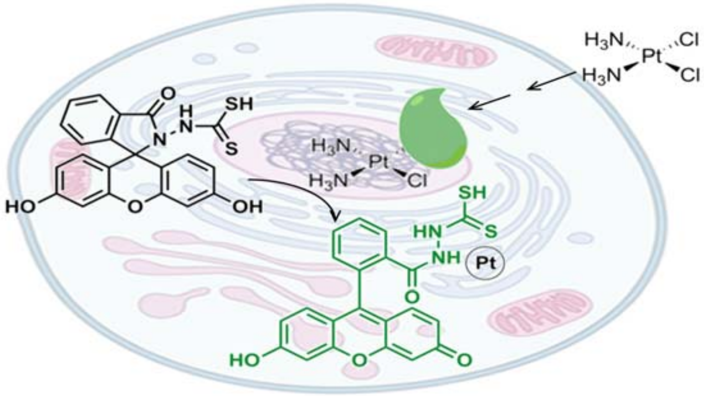
The interaction of non-essential transition metals with biological systems is of considerable interest. These transition metals are of significance not only as potential toxic metals, but also as therapeutic agents.

With the growing prevalence of antibiotic resistance, the historical use of silver as an antimicrobial agent has received renewed interest. Silver complexes and nanoparticles have shown good efficacy with a broad spectrum of action. The mechanisms of toxicity, cell penetration, bioaccumulation and metabolism of these silver species, however, are not well understood. Similarly, platinum complexes have been used as a chemotherapeutic agent for over thirty years, but there remain many questions about their mode of action and metabolic processing. These deficiencies in understanding are largely due to a lack of tools that can provide specific information with sufficient spatial resolution.

As these metals are poorly understood in a clinical context, we have developed small molecule fluorescent sensors that offer a straight forward and practical alternative to existing absorbance methods. Here we describe our novel fluorescent probes to detect and quantify biologically-important heavy metals including silver and platinum.



From Complexity to Simplicity: Innovative Strategies for Natural Product Synthesis

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ABSTRACT TEXT

The high affinity of phosphinogold(I) complexes to alkynes and allenes combined to excellent photoluminescent properties dimeric gold complexes have provided a new platform for the discovery of unique and innovative transformations in organic synthesis. In this context, the development of novel gold-catalyzed processes and their applications to the synthesis of complex natural products will be presented.

FTIR-based sensing of hydrocarbons in water under extreme conditions

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A polymer-coated attenuated total reflectance (ATR) crystal in conjunction with Fourier transform infrared (FTIR) spectroscopy has been previously used for the detection of dissolved hydrocarbons in water. The polymer is typically hydrophobic and rubbery in order to enhance hydrocarbon sorption while minimizing wateruptake. The evanescent wave travelling along the ATR crystal interacts with hydrocarbons that partition into the polymer membrane/film and the spectroscopic signature for the hydrocarbons is obtained providing the transduction mechanism for the sensor. To date, there has been very little or no published work using this approach at elevated pressure/temperature conditions. Subsequently, the influence of pressure and temperature on the hydrocarbon-polymer partition process is not known and further work is needed to characterize this process before sensor measurements can be made under a range of harsh environmental conditions. Using a ruggedized fibre optic based probe with a diamond ATR tip, we have conducted high pressure/temperature (up to 250 bar and 80°C) experiments with ppm level concentrations of toluene and naphthalene dissolved in water. We have shown that there is minimal influence on the sensing properties due to changes in pressure. However, at higher temperatures, the sensitivity decreases presumably due to diminished partitioning of the hydrocarbons from the water phase into the polymer phase (as predicted by equilibrium theory for exothermic processes). The ability to detect at hydrocarbons in water at these extreme conditions will widen the range of potential applications for this technology.

Fundamental understanding and applications of spinifex cellulose nanofibres

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ABSTRACT

Cellulose represents the most abundant renewable polymer on Earth. Its earliest human use dates back thousands of years, with extensive utility today in products such as paper, cellophane, explosives, textiles and dietary fibres[1]. Confirming the hypothesis that extreme environments drive the evolution of plants with unusual material properties, we discovered that Australian arid spinifex grass is a unique source of very flexible cellulose nanofibres (CNF) of high quality and yield (50-70%). In the international nanocellulose research community there is a growing awareness that different biomass sources can have very specific advantages when it comes to the resultant CNF property profiles achieved. As part of this trend, attention is shifting to non-wood sources, and our work on spinifex is one of the most differentiated examples to date. We have clearly demonstrated_ENREF_1_ENREF_1[2-4] that from *T. pungens* spinifex we can readily isolate high aspect ratio CNF with an average width of 20 nm after pulping with simple mild sodium hydroxide treatment and with as little as just one pass through a high-pressure homogeniser at relatively low pressure, thereby drastically reducing energy demand and cost of production[4-5]_ENREF_19. An unusually high remnant hemicellulose content of approximately 30-40%[3] appears to be an important factor in this more amenable CNF fibrillation trait. This presentation will give an overview of the fundamnetal underestanding of spinifex nanofibre structure and our team research and technology development activities related to spinifex nanofiber production, with potential applications including filtration membranes, polymer composites and low cost, renewable carbon fibres.

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Gating Electron Transfer in Peptides Towards Molecular Switches

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Electron transfer in proteins plays a crucial role in energy conversion and storage processes in all living organisms, thus providing an opportunity to mimic nature for applications in bio-inspired molecular electronics. However, the vast complexities of such systems is somewhat limiting to progress, with model synthetic peptides presenting as ideal alternatives in this context. Here, electrochemical studies are reported on a series of peptides to determine the influence of different side-chains and backbone rigidity on electron transfer, to progress the field of molecular electronics. Specifically, these peptides share either a common helical or β-strand conformation to cover a range of secondary structures, to fully investigate the influence of backbone rigidity. Two types of side-chain tethers, either triazole-containing or alkene-containing, are also compared to investigate these effects on electron transfer. Our results showed that the observed formal potentials (E_o) and apparent electron transfer rate constants (k_{et}) fall into two distinct groups. The peptides constrained via a side-chain tether exhibited high formal potentials and low electron transfer rate constants, whereas the linear peptides displayed low formal potentials and high electron transfer rate constants. This was found to occur irrespective of the backbone conformation, or the nature of the side-chain constraint. The vast formal potential shifts (as much as 482 mV) and the large disparity in the electron transfer rate constants (as much as 97%) between the constrained and linear peptides, provides two distinct states (i.e. on/off) with a sizeable differential, which is ideal for the design of molecular switches.

Generalising Marcus-Hush Theory to the Transfer of Delocalised Charges

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Many important systems, from photosynthetic complexes to organic photovoltaics, consist of molecular aggregates of charge donors and acceptors. Marcus-Hush theory (MHT) can describe the rate of charge transfer in molecular systems, but only if the charge is transferred from a single donor molecule to a single acceptor molecule. However, within many molecular systems, charges are delocalised across multiple molecules, making MHT inapplicable. The only alternative are simulations that treat the aggregates as supermolecules, but these suffer from poor scaling with system size and from the need for a complete recalculation if a small change is made to a part of the system.

Here, we describe charge transfer between delocalised aggregates (Figure 1), with the advantage that the inter-aggregate transfer rate can be calculated based on the known properties of the individual molecules and the couplings between them, obviating the need for large-scale simulations.

We also discuss potential applications of our approach to the study of photosynthetic reaction centres, organic photovoltaics, and metal-organic frameworks.

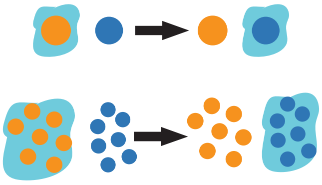

Figure 1. **Top:** Marcus-Hush theory describes the transfer of a charge (pale blue) from a donor molecule (orange) to an acceptor molecule (dark blue). **Bottom:** generalised Marcus-Hush theory describes the transfer of a delocalised charge from an aggregate of strongly coupled donors to an aggregate of acceptors.

GLOBAL HEALTH RISK ASSESSMENT FOR DISINFECTION BYPRODUCTS (DBP) DUE TO CHLORINE IN DRINKING WATER

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ABSTRACT TEXT

Chlorine is used to disinfect drinking water in many countries throughout the world. However chlorine reacts with drinking water components to produce a range of disinfection byproducts (DBP). The exposure dose for each of the major disinfection byproducts (EXP_D) was calculated from literature data from more than 10 countries and plotted as cumulative probability. These plots were compared with threshold Human Equivalent Dose (HED) from surrogate animals representing the threshold for adverse effects. The highest human EXP_D was lower than the threshold HED for triclhloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). All the threshold HED values for surrogare animals were approximately 10^2 to 10^4 higher than the exposure dose in drinking water (EXP_D). On the other hand the probability plots for exposure to DBPs were compared with the human epidemiology data for these compounds calculated as the Life Time Average Daily Dose ($LADD_H$). The highest EXP_D exceeded the threshold $LADD_H$ representing the threshold dose-response values for adverse effects for TCM, BDCM, DCAA and TCAA. This suggests that there are possible adverse health risks which in the epidemiological investigations were effects such as cancers and developmental effects on humans. This suggests that a proportion of the human population, represented by the published data from the 10 countries considered, has a risk of adverse health effects

Glyco-coated Micelles and Liposomes to Treat Intracellular Infections

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Chronic bacterial infections are still difficult to eradicate as bacteria are capable of surviving in infected host cells although antibiotics are used comprehensively to treat these infections. The clinical failures of antibiotics are associated with low bioavailability, poor penetration capacity to bacterial infection sites, their side effects, and the antibiotic resistance properties of bacteria.[1] Moreover, many deadly infectious diseases such as tuberculosis, listeriosis, salmonellosis etc. are produced by intracellular bacterial pathogens. The intracellular location of these pathogens protects them from the host defense systems and from some antibiotics with poor penetration into macrophages.[2] Therefore, the use of non-viral antibiotic delivery systems (ADS) is receiving considerable attention to improve the penetration of drugs into macrophages. This presentation will describe the preparation of liposomes and micelles using glycolipids and natural polysaccharides, respectively. Initially, we targeted macrophage mannose receptors (MMR) and macrophage inducible c-type lectins (Mincle) by covalently linked multivalent mannose and lipo-mannose on the surface of liposomes and micelles. Cholesterol and 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC) were used to prepare the liposomes and cationic polysaccharides chitosan was utilize to make micelles. Aminoglycosides and decanesulfonylacetamide (DSA) antibiotics are then utilized to encapsulate into the nano-carrier system in order to deliver the payloads. Both the carrier systems were investigated against human (U937) and mouse (RAW 264.7) macrophages by measuring the cellular uptake and released cytokines. The results show the excellent uptake behaviours of the sugar coated vehicles compared to control and significant modulation of the release of TNF-α and IL-6 upon treatment of LPS-stimulated macrophages with the formulations.

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GOLD-CATALYSED REACTIONS OF C-C MULTIPLE BONDS

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ABSTRACT TEXT

In the literature, two major mechanisms have been proposed for gold-catalysed formation of C-C bonds with unsaturated substrates: inner-sphere syn-addition and outer-sphere anti-addition (a Friedel–Crafts-type mechanism). In this work, the $AuCl_3$-catalysed hydrofurylation of allenyl ketone, vinyl ketone, ketone and alcohol substrates has been investigated with the aid of density functional theory calculations and it is found that the corresponding functionalisations are best rationalised in terms of a novel mechanism called "concerted electrophilic ipso-substitution" (CEIS). We suggest [1] that the gold(III)-furyl σ-bond produced by furan auration acts as a nucleophile and attacks the protonated substrate via an outer-sphere process. This unprecedented mechanism needs to be considered as an alternative plausible pathway for gold(III)-catalysed arene functionalisation reactions in future studies.

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Gold-Catalyzed Reactions Involving Functionalized Carbene Intermediates

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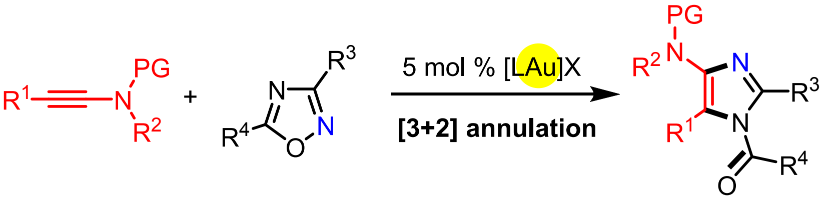
Triggered by new reactivity patterns discovered in 2000,[1,2] has become a very successful sector of catalysis research.[3] After methodology development and mechanistic studies[4] in the last years applications in total synthesis became a hot topic in gold catalysis.[5]
Typical intermediates would be vinylgold/arylgold species or gold carbene species,[3,6] recently also gold vinylidene intermediates.[7,8] In 2013 as a third mechanistic principle photoredox catalysis with gold complexes evolved, here after pioneering work of Barriault and Gagosz[9] our group also contributed catalytic cycles involving gold(I) and gold(III).[10]
Gold-catalyzed reactions involving functionalized gold carbene intermediates represent another significant variation of the reactivity patterns of gold catalysis. These new reactivity patterns will be discussed in detail, the presentation will combine experimental and computational results.



23 examples with yield up to 93%
100% atom economy
gram-scale synthesis

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GRADUATE EMPLOYABILITY: OUTCOMES OF AN INTERVENTION

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Graduate employability is an important issue for higher education as the global financial crisis has led to a significant decline in the employment prospects of new graduates over the past few years. This issue is additionally important due to the reported dissatisfaction of many employers with graduates' ability to contribute effectively to the workplace. This research seeks to address these problems by exploring the skills needs of recent science graduates and their employers, and designing interventions that will inculcate such skills and attributes into undergraduate students via the curricula. In this presentation, we report on the outcomes of an intervention designed to address the skills needs and analyse if it had any impact on students' notions of employability. The intervention, conducted as a day-long workshop, was delivered to three groups of third- and fourth-year students. We used quantitative data to track possible differences in students' self-perceptions of their employability following participation in the intervention. In addition, qualitative data, collected through students' reflective notes, provided insights into how they perceived the value of the intervention in improving their self-perceived employability. Both data types indicate a positive impact of this type of intervention on students' perception of their employability and related underpinning skills. Our findings call for a broader integration and evaluation of targeted 'employability' workshops into senior undergraduate or capstone-style curricula.

Graphene quantum dots (GQDs) based aptasensor toward intracellular cytokine monitoring

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ABSTRACT:

The detection of cytokines in body fluids, cells, tissues and organisms continues to attract considerable attention due to the importance of these key cell signalling molecules in biology and medicine. Measurement sensitivity is always an issue for cytokines because they are released into the extracellular milieu resulting in molecular dilution at pg/mL levels (in the pM range). Thus, it is essential to develop a simple and sensitive cell-surface sensor that affords comprehensive characterization and quantitative analysis of cytokines secreted from live cells. Aptamer based structure-switching biosensing methodology has great potential for real-time sensing of small molecules. We developed an aptasensor being able to dynamically and specifically capture ultra-small amount of cytokines. Cytokine aptamer modified graphene quantum dots (Ap-GQDs) and epitope modified GQDs (Ep-GQDs) were prepared, respectively. The mixture of Ap-GQDs and Ep-GQDs is fluorescence “OFF” due to the self-quenching of GQDs, which can be used as the probe for sensing cytokine intracellularly. The presence of cytokines in cells could displace away epitope and bind with aptamer, resulting in the dissociation of Ap-GQDs and Ep-GQDs bioconjugates and turning “ON” fluorescence. Ap-GQDs and Ep-GQDs bioconjugates were characterised by TEM, electrophoresis, fluorescence and cytotoxicity assay. The aptasensor was used to monitor intercellular cytokine IFN-γ secretion with high sensitivity (0.1 pg/mL). The designed sensing mechanism was very simple and universal, and it could be used for detection of a broad spectrum of cell-secreted molecules in a dynamic manner. It was also essential for understanding cell biology and pathway of cytokine secretion in live cells.

Graphene-Oxide Stabilized Polymer Nanoparticles: A Route to Hybrid Materials

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ABSTRACT:

Graphene oxide (GO), the oxidized form of graphene prepared by the oxidation and exfoliation of graphite, is considered the most promising route towards the preparation of polymer-graphene composite materials.[1-3] GO possesses numerous functional groups for further reaction, can be dispersed in polar media, and is compatible with many polymers. Additionally, GO can be reduced to graphene post-functionalization using a variety of techniques, yielding a material with impressive mechanical, electrical and thermal properties.

Our group has focused on the recent discovery of the amphiphilic nature of GO, which has been shown to behave as a 'surfactant' for stabilization of oil-in-water (o/w) emulsions (a Pickering emulsion).[2,4] We have used the surfactant-like nature of exfoliated GO sheets with very small lateral dimensions (~ 30 nm) to prepare 'armoured' polymer nanoparticles by miniemulsion polymerization, where GO sheets are driven to the monomer droplet interface, forming a 'shell' on the particle surface after polymerization. We have demonstrated the applicability of this method for styrene,[5] divinylbenzene, members of the (meth)acrylate family,[6] copolymerization systems, and the preparation of hollow capsules.[7] More recently we have investigated encapsulation or reduced GO in poilymer nanoparticles and poly(ionic liquid) stabilization.[8,9] We consider this a highly convenient route towards the preparation of polymer-graphene composites for numerous applications, including polymer thin films, encapsulation of catalytic nanoparticles and energy storage.

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HEALTH RISK ASSESSMENT OF MOUNT ISA POPULATION FROM LEAD EXPOSURE

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The Lead Pathway Air Study (2007-2012) shows human exposure to lead at Mount Isa using the enHealth (2012) risk assessment framework and sophisticated analytical techniques. Human exposure to lead is from ingestion of <250 µm sized particles via the digestive system and inhalation of <10 µm sized particles into lungs; absorption via skin is insignificant. Extensive sampling of the mine site and houses provided physico-chemical characteristics using synchrotron-based X-ray absorption spectroscopy (XAS) for lead speciation/composition, high resolution lead isotope measurements and other techniques (XRD, SEM and particle size analysis) to describe multiple sources. Bioavailability testing on 10 composites using rats was correlated with bioaccessibility on <250 µm fractions using PBET (physiologically-based extraction test) simulating the human digestive tract. Lead solubilised in the stomach is transferred with food nutrients to the intestine where absorption occurs. Average pH with fast, semi-fed and full-fed states of the stomach and near neutral intestine pH provided an intermediate pH for PBET testing. Inhalation is <5 % of total exposure for people living in Mount Isa, while ingestion is >95 %. PM_{10} air particulates exiting Mount Isa smelter stacks were not the major source of human lead exposure via inhalation in Mount Isa city for this sampling. Ingestion of <250 µm diameter dust is from ground deposition; lead isotope ratios showed lead originated from mine Urquhart Shale and city area outcrops. Lead isotope ratios show origin of lead regardless of chemical form while XAS gives chemical form; XAS shows differences even for similar lead isotope ratios.

Helical Porphyrin Oligomers Inspired by Biological Architectures

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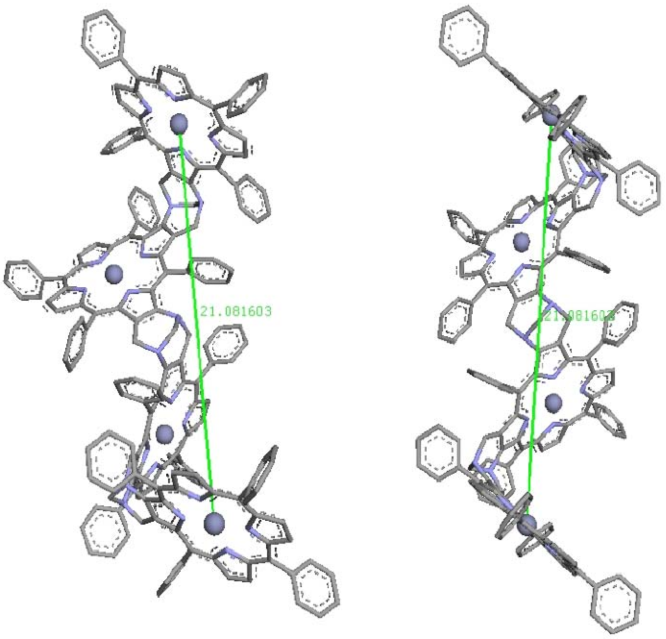
Helical structures are found throughout Nature where they play an important role in self-replication and scaffolding motifs. When combined with chirality, as in DNA, molecular specificity is imparted which is critical in information transfer as well as providing the basis for evolution where order is derived from chaos.[1] Herein we report the synthesis of a regiospecific helical porphyrin array **1** where the *C*$_2$ symmetry of the Tröger's base linker is utilized to induce a twist, and hence the prospect of a helical arrangement of porphyrin macrocycles, within the oligomer. In addition, the chirality imposed by the Tröger's base linker can readily be exploited, as the facile isolation of its constituent enantiomers[2] will enable stereospecificity to be incorporated into a tailored reaction sequence. Hence it is envisaged that a wide variety of molecular motifs with defined inter-macrocyclic distances and orientations can be generated. Photonics and host-guest chemistry are potential applications of this work.



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Heteroaromatic natural product synthesis enabled by Ir-catalysed C-H borylation

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The vast majority of heterocycle syntheses are defined by a cyclization reaction that is typically the key synthetic step. A conceptually disparate approach to this traditional methodology would be to subject a simple, readily available heterocyclic scaffold to sequential C-H functionalization reactions,[1] thus avoiding any cyclisation steps. We have found the iridium-catalysed C-H borylation[2] to be successful in this regard and some ongoing natural product syntheses using this approach will be discussed.

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High efficiency microextraction techniques

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When investigating analytes present in samples at low concentration, in the ppb or ppt range, a pre-concentration technique must be incorporated into the sample preparation protocol before analysis. There is a therefore a major drive to improve pre-concentration techniques[1] to remove influences of the matrix (e.g. tissue samples, plant specimens, food samples) that compromise data integrity. A second area of intense research is to miniaturise the pre-concentration technique, to reduce financial and environmental costs[2] and the amount of sample specimen required.[3]

We have developed the bubble-in-drop single drop micro-extraction technique,[4] which offers unexpectedly high levels and rates of pre-concentration of a range of analytes, from triazine herbicides[4] to synthetic growth hormones for cattle,[5] and which is suited to environmental monitoring.[6] More recently,[7] we developed a solvent-assisted headspace sampling method, using solid phase microextraction, which facilitates unprecedented volatilisation of pollutants such as phenols. The presentation will briefly cover these two methods (Figure 1).

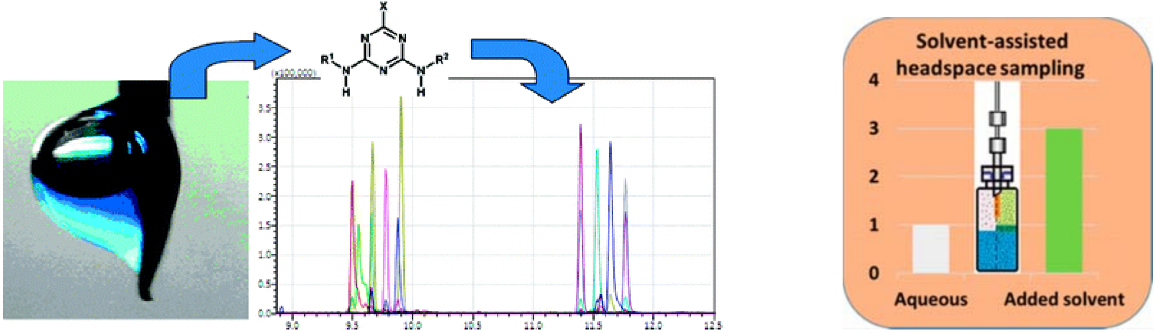

Figure 1

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Highly efficient Al(OTf)$_3$-catalysed organic transformations: domino carbohydrate chemistry

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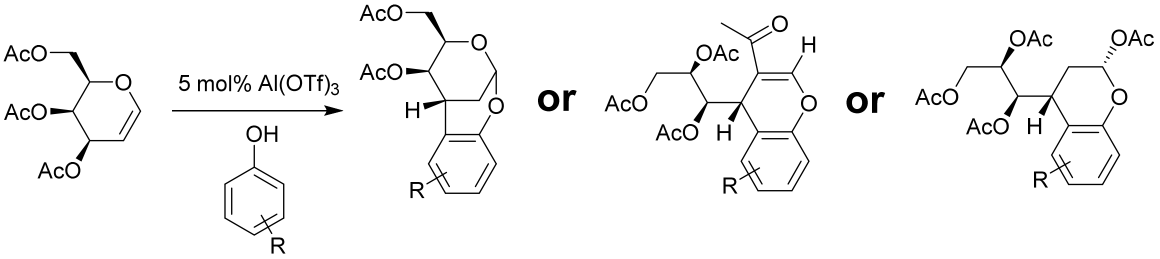
Lewis acids play a central role in the catalysis of co-catalysis of a wide range or organic chemical transformations. Metal triflates, especially lanthanide triflates, have become highly developed as a new type of Lewis acid with improved properties over traditional counterparts.

Aluminium triflate was largely overlooked as a Lewis acid catalyst until our work in this area demonstrated its superior activity as a catalyst for a wide range of reactions. These include ring-opening reactions,[1] atom efficient protecting group chemistry[2] and Pd-catalysed carbonylation reactions,[3] where the Al(OTf)$_3$ is a co-catalyst. More recently, we have discovered highly efficient transformations of carbohydrates into structurally diverse bi- and tricyclic compounds with defined stereochemistry (Scheme 1).[4] These discoveries and recent work will form the focus of the presentation.



Scheme 1

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HIGH-TEMPERATURE MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SEPARATION OF TRIACYLGLYCEROLS IN OLIVE OIL

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The separation of triacylglycerols (TAGs) in complex samples has always been a problem, even by using liquid chromatography. A ‘heart-cut’ multidimensional gas chromatographic (H/C MDGC) method is developed to separate olive oil TAGs. A relatively short non-polar first dimension column (^{1}D) and a mid-polar second dimension column (^{2}D) with high temperature limits (350 °C) were used for the separation. The ^{1}D displayed three major groups of peaks in a ratio of approximately 5:33:62, with increasing retention. Several – about 3 – minor groups were located between these. H/C of the minor peaks and sampled regions of the major peaks eluting from the ^{1}D outlet were cryotrapped at the ^{2}D inlet. The GC oven was cooled down and the trap was released prior to the temperature programmed ^{2}D separation. On the ^{2}D separation, each of the H/C zones gave 2 to 5, and in some cases even more separated peaks of TAGs. Flow optimisation on the ^{2}D after the release of the trapped TAGs resulted in better separation as well as an increased number of displayed peaks. Six ‘heart-cuts’ from different regions of peaks from the ^{1}D were simultaneously trapped and released to the ^{2}D resulting in more than 22 separated peaks of TAGs. It was found that different TAGs could be revealed for each of the 3 major groups, by H/C sub-sampling across the peaks. This tandem column strategy appeared to resolve more components than that usually observed on a single column.

Hybrid hydrogels for medical applications

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An important goal of tissue engineering is to replace extracellular matrix (ECM) with artificial scaffolds that can be synthesized in mild and biocompatible conditions, introduced to the specific site of interest and used to feed the cells for their growth and proliferation. Despite the substantial progress that has been made in biomaterials synthesis and functionalization, the challenge of mimicking the ECM with implants that are able to reduce immunoresponse is still unmet.

Recent findings have shown that mesenchymal stem cells (MSC) infiltrating into the implant have effects on the scaffold integration by improving the healing process.

Towards this aim, herein we report a novel biocompatible hydrogel with the ability to release an MSC migration-inducing factor, the chemo-attractant Stromal cell-Derived Factor-1α (SDF-1α), for the recruitment of stem cells.

In particular, we synthetized a polyamidoamines-based nanocomposite hydrogel, cross-linked with mesoporous silica nanoparticles that can function as nanocontainers for the release of SDF-1α from their pores, to address the cells. The hydrogel proved to provide optimal structural support for MSC infiltration and proliferation and chemotaxis of MSC *in vitro* was investigated with a dual hydrogel system. Subcutaneous implantation of SDF-1α-releasing hydrogel in mice resulted in a modulation of the inflammatory and fibrotic reaction *in vivo*, suggesting an improvement of the tissue response towards the implant.

Encouraged by these results the hybrid hydrogels have also been injected in the stomach of pigs with the final aim to study the gelation kinetic *in vivo*.

Hybrid Materials for Selective Actinide and Lanthanide Separations

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ABSTRACT

Selective separation of actinides and other radioisotopes from complex media is a highly important challenge in the context of environmental remediation, mining and industrial processing. This research is focussed on development of advanced materials that are able to selectively extract actinides and/or lanthanides from acidic solutions. Traditionally, actinide separation processes are based on liquid-liquid extraction. However, use of solid phase sorbent materials has several advantages such as the lack of organic solvent wastes.

Framework materials based on titania and zirconia have been developed and functionalised with organic ligands in order to impart selectivity. Titania and zirconia based framework materials were chosen due to their radiolytic and hydrolytic stability, as well as the fact they can be easily converted to transmutation matrices or wasteforms once they are loaded with actinides. The framework materials used vary in complexity from simple nanoparticles to millimetre sized, spherical, hierarchically porous beads with ordered mesoporosity. The bead morphology is desirable as it allows close packing in chromatographic columns with minimal clogging facilitating improved ease of handling. In addition, bead-based sorbent materials typically offer improved loading capacity over nanoparticles due to their higher surface areas. The presence of ordered porosity of bead-based sorbent materials can also improve sorption kinetics.

In terms of organic ligands to impart selectivity, functionalisation with phosphonates, peptides and bistriazinylpyridine (BTP) has been performed. Using phosphonates or peptide functional groups, selectivity for lanthanides was demonstrated. Using BTP functionalized materials, the more challenging minor actinide-lanthanide separation could also be achieved.

Hydrophobic Interactions & Surface Forces in Petroleum and Mineral Engineering

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Hydrophobic effects play important roles in a wide range of natural phenomena and engineering processes such as coalescence of oil droplets in water, air flotation of mineral particles, folding and assembly of proteins and biomembranes. The intermolecular and surface interactions at solid/oil/water/bubble interfaces play critical roles in many industrial processes such as oil production. In this talk, I will highlight our experimental attempts to reveal the physical origin of hydrophobic effects by directly quantifying the hydrophobic interaction on both solid/water and fluid/water interfaces, and then report our recent progress in probing the interaction mechanisms of deformable water-in-oil (W/O) and oil-in-water (O/W) emulsion droplets and air bubbles using state-of-the-art nanomechanical techniques such as surface forces apparatus (SFA) and atomic force microscopy (AFM) coupled with bubble/drop probe & interferometry techniques. Micropipette and in-house built 4-roll mill fluidic device were applied to monitor the stability of both pipette-supported and freely suspended emulsions in the presence of asphaltenes (the heaviest component in bitumen and crude oil) under quasi-static and dynamic flow conditions, respectively. The interaction forces between O/W or W/O emulsion drops in the absence and presence of asphaltenes were directly measured using droplet probe AFM and analysed using a theoretical model based on Reynolds lubrication theory and augmented Young-Laplace equation by including the effects of disjoining pressure. Our results provide useful insights into the fundamental understanding of hydrophobic interactions and interaction mechanisms of deformable emulsion droplets & air bubbles in complex fluids, with implications in related processes in oil production and mineral engineering.

HYDROTHERMALLY STABLE, THIN FILM SULFATED ZIRCONIA CATALYSTS FOR BIOMASS CONVERSION

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Biomass offers the most readily implemented, and low cost solution for carbon neutral transportation fuels, and the only non-petroleum route to organic molecules for the manufacture of bulk, fine and speciality chemicals. Platform chemical and fuel production from the aqueous phase transformation of sugars derived from waste cellulose hydrolysis is attracting significant interest but requires the availability of hydrothermally stable heterogeneous catalysts with bifunctional active sites. Here we report on the synthesis and application of conformal zirconia and sulfated zirconia catalysts deposited on mesoporous SBA-15 for the conversion of bio-based molecules to fuels and chemicals. The amphoteric properties of zirconia make it an attractive catalytic material to employ as a bifunctional catalyst with acid-base character, with judicious control over sulfate loading enabling systematic control over the surface Lewis–Brønsted acid and base properties. Such bifunctional solid acid-base catalysts are attractive to facilitate efficient conversion of glucose to 5-hydroxymethylfurfural (5-HMF); a valuable chemical intermediate to produce linear alkanes for diesel and jet fuels, and building blocks for the synthesis of diverse solvents, polymers and plastics. Zirconia doped with sub-monolayer SO_4 coverages offer the ideal balance of basic and Lewis/Brønsted acid sites required to respectively isomerise glucose to fructose, and subsequently dehydrate fructose to 5-HMF. The design of such bi-functional catalysts capable of effecting one-pot telescopic syntheses in aqueous media will become increasingly critical to achieve atom-economical, selective transformations of bio-derived molecules for sustainable chemicals and fuels.

Illuminating biological microenvironments

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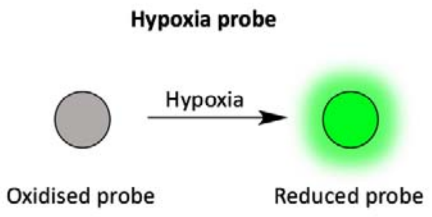
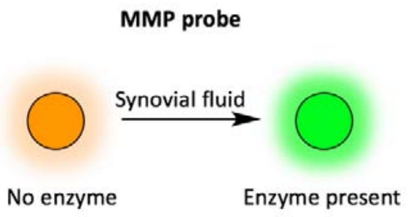
Fluorescent probes now find widespread use as biological tools. They can be used to monitor live systems as dosing is minimally invasive, and biological events can be captured in real time using reversible probes. Low concentrations of analytes can be monitored using reaction based probes, as the fluorescence signal builds up over time and is amplified. Comparison between samples can be measured using ratiometric probes, which provide better quantitative data as two wavelengths can be monitored, to give a ratio independent of probe concentration.

Fluorescence probes are useful for visualising biological microenvironments such as redox state, ion concentration, hypoxia and enzyme levels. For example, hypoxia is often seen within solid tumours, redox state can be altered during inflammation, and some enzymes catalyse deleterious reactions that lead to disease.

We have developed probes for metalloproteinases; enzymes which can cause disease by degrading collagen, which makes up 90% of the protein in cartilage and 95% of the protein in bone. Metalloproteinase plays a role in the progression of arthritis, a condition that leads to degeneration of joints. In the body, collagenases can be secreted into the synovial fluid surrounding joints by fibroblasts.

We have also developed probes for hypoxia, which is a deficiency of oxygen in tissues. Hypoxia is common in solid tumours, as growth may block and damage blood vessels. Tumour spheroids are useful for modelling hypoxia as their growth can prevent oxygen from diffusing to the centre of the spheroid. We have tested our probes in monolayers and spheroids.





Improved Method for Analysis of Tritium in Landfill Leachate

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Tritium (^{3}H, $t_{1/2}$ = 12.32 years) is a natural radioactive isotope of hydrogen produced by cosmic radiation. However, enhanced global anthropogenic concentrations in the environment have resulted from thermonuclear weapon detonations, releases from nuclear facilities and due to its applications in medical, research and military industries. Further localised anthropogenic sources have been linked to industrial and municipal waste resulting from the interaction of groundwater with waste containing ^{3}H such as luminous components of watches and signs.

^{3}H associated with the water molecule moves similarly to water and can be used as a conservative tracer for leachate movement in groundwater surrounding municipal and industrial waste sites. ^{3}H measurement is usually undertaken using Liquid Scintillation Counting (LSC). However, landfill leachate is often very dark in colour, high in organic compounds and sometimes alkaline, which can lead to colour and chemical quenching during the LSC measurement.

This paper describes the development and testing of a new sample pre-treatment method that aims to eliminate organic compounds, adjust pH for optimal interaction with the Eichrom® Tritium column and remove colour prior to LSC.

This improved method has been applied to leachate from various landfill sites within Australia in order to establish ^{3}H levels and study groundwater movement and/or to differentiate different sources of groundwater in sites potentially affected by landfill leachate.

Incongruent Focuses on Employability Between STEM Students and STEM Employers

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Tertiary STEM educators face significant challenges in preparing students for gaining and then maintaining employment in STEM field. Within the university curriculum, the relationship between discipline-based learning and employability is poorly understood, and STEM graduate outcomes are characterised by mixed results despite a strong STEM skills demand in the workforce. We address these challenges by identifying the relationship between discipline-based learning and employability, followed by a comparison between STEM students' and employers' focuses on employability development.

We conducted a study on final year capstone unit students in the STEM faculty at Macquarie University (N=492). This presentation focuses on findings of the cluster of disciplines of Chemistry, Chemical and Biomolecular Sciences, and Biological Sciences (n = 145). A parallel, concurrent STEM employer and industry stakeholder study was also conducted (n = 62). By applying the Career Information Literacy Learning Framework (CILLF) we link employability with generic, discipline-based and transformative learning. Career Information Literacy (CIL) is the ability to search, evaluate and synthesise information to foster self-understanding, opportunity awareness and ultimately create one's own knowledge for work and life decision-making.

Through profile analyses, we found these students differ significantly from STEM employers/industry stakeholders in their respective emphases on employability. Students focus on discipline-specific knowledge and skills while employers focus on transformative qualities which transcend discipline boundaries. Implications and limitations of the findings are discussed with recommendation for further investigation.

Influence of Triblock Copolymer on Processing Electroactive Polymeric Fibers

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Nanocomposite fibers have shown tremendous potential as electroactive and biocompatible materials. While polymers are normally insulating conductive polymers can be obtained by incorporating carbon nanotubes. Electroactive composite fabricated into nanofibers have shown to be effective as carriers of therapeutic agents and also as active components in biosensor. Previous investigations in our group used functionalized and processable electroactive nanofibers to study polymer-biomarker interactions. These nanofibers can be conveniently prepared by electrospinning process. Variables affecting the quality of nanofibers include solution viscosity, polymer molecular weight, and polymer type. The polymer matrix concentration, and microphase separation in the nanofibers contribute to the overall physical characteristics of the nanofibers. In this study, we investigate a novel thermoplastic elastomeric triblock copolymer as an additive to prepare single wall carbon nanotube (SWCNT) based fibers with significantly improved physical and morphological properties.

The triblock copolymer poly(styrene)-b-poly(dimethylsiloxane)-b-poly(styrene) (PS-b-PDMS-b-PS) was synthesized by living anionic polymerization. Each block was 10K in molecular weight. A solution with PS-b-PDMS-b-PS/PS at a various w/w ratios in DMF along with SWCNT at 1% wt was electrospun onto a silicon wafer at a flow rate of 20μl/min and a potential of 10kV. The fibers were characterized by scanning electron microscopy. Current-voltage plots of the fibers were obtained using a four-point probe. A solution with a ratio of 100:1 of both PS 900,000 Mw/SWCNT and PS-b-PDMS-b-PS/SWCNT was also spun and for comparison.

Inorganic-doped Conductive Polymer Hybrids for Thermoelectric Energy Conversion

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Hybrid organic-inorganic materials integrated from soft organic molecules or polymers with hard inorganic multiple compounds have played a major role in the development of functional materials. These materials demonstrate broad potential and application in many emerging areas including energy and environmental due to their tunable chemical structures, integrated performance and excellent compatibility to different conditions. In this presentation, we will present our current progress on hybrid organic-inorganic conductive films for thermoelectric applications. Some of the materials have been prepared by doping inorganic structures into organic polymers, in-situ formation, as well as post-modification procedures. Some of them demonstrate moderate to high electric conductivity (> 300 S/cm) and seebeck coefficiency (> 100 μV/K). Some challenges in this study, such as the optimization of materials structure and performance, shall also be discussed.

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INSTANT FUNCTIONALIZATION OF GOLD NANOPARTICLES WITH THIOLATED FUNCTIONAL NUCLEIC ACIDES WITH HIGH STRUCTURE INTEGRITY

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Functional nucleic acids (FNAs) such as molecular beacons, aptamers and DNAzymes require the well-defined secondary structures to be functional. The conformation controlled attachment of thiolated FNAs to gold nanoparticles (AuNPs) is critical for many applications including bio-sensing, bio-imaging, drug delivery, and nanostructure assembly, however, is proved to be quite challenging. The current methods either need a long incubation time (1-2 days) or surfactants or a low pH buffer. These conditions are not suitable for the immobilization of thiolated FNAs. Serious or partial aggregation of the colloids was commonly observed when these approaches were used, suggesting that the secondary structures were hardly to be controlled and the undesired interactions occurred between FNAs on different AuNPs. We report here a novel method using oligoethylene glycol as a spacer to shield the electronic repulsion between AuNPs and nucleic acids and therefore to substantially speed up the interaction between gold and thiol. Our method enables the attachment process finished in two minutes under neutral pH. Taking molecular beacon (anti-HVB probe), AS1411 (anti-cancer cell aptamer), and EAD2 (DNAzyme with peroxidase activity) as three typical examples, we demonstrated that the prepared complexes maintain the thermodynamic stability, the structure integrity, and the functions as well. Our work suggests that oligoethylene glycol spacer is a highly effective parameter to tune the nucleic acid adsorption kinetics and thermodynamics besides pH and salt, providing a novel means to enable the more controllable and versatile functionalization of AuNPs.

Intersystem Crossing is Important in Small Carbonyl Systems

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Formaldehyde is a key organic component of the atmosphere. Understanding its photochemistry is critical to understanding the chemistry of the atmosphere. Current models ignore much of its ground state chemistry by assuming collisional cooling is faster than internal conversion or intersystem crossing, deactivating the molecule before it reaches its ground state. However, experimental and theoretical evidence suggests this is not the case (Fu 2011, Hobday 2013). I will present compelling results from high-quality spin-orbit coupling calculations and multi-configuration time-dependent Hartree calculations showing that intersystem crossing in formaldehyde is fast, and allows the molecule to return quickly to S_0. These time scales are fast enough for interesting ground state chemistry to be possible in the atmosphere. This fast intersystem crossing is driven by high T_1-S_0 spin orbit coupling, which is a consequence of the orbital structure of the carbonyl group. Subsequently this result should be common to all carbonyl-containing compounds.

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Intravenous Therapeutic Genome Engineering Using Dendronised Polymers

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ABSTRACT

The field of genome engineering has revolutionized our current understanding of how genotype influences phenotype, especially in the field of cancer biology. Cancer is a disease characterized by multiple genetic and epigenetic alterations in oncogenes and tumour-suppressor genes. Using sophisticated genome engineering tools like the clustered regularly interspaced short palindromic repeat (CRISPR) associated protein (CRISPR/Cas9) we can now directly edit or modulate the function of DNA sequences in their endogenous context, enabling identification and correction of causal genetic variations. However, a major stumbling block in this field has been efficient delivery. Effective CRISPR-based genome and epigenome engineering can only be achieved *via* concurrent delivery of multiple components to cells. These include the Cas9 or dCas9 components and multiple short guide RNAs (sgRNAs). All of the efforts aimed at the concurrent delivery of these components to cells using non-viral methodologies so far have failed. Currently transfection can only be achieved using high-capacity adenoviruses, electroporation and hydrodynamic injection-based delivery, albeit with lower efficiencies, a restricted range of accessible targets, and associated immunogenicity. In this presentation we report a novel medically relevant and translatable approach using polymers for enabling targeted CRISPR delivery in a highly relevant *in-vivo* model of breast cancer.

IONIC LIQUID-BASED REDOX ELECTROLYTES FOR THERMAL ENERGY HARVESTING

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Thermoelectrochemical cells are increasingly promising devices for harvesting waste heat, particularly at temperatures <200 °C, such as from power plants or geothermal sources. This technology offers the promise of continuous and cheap operation, with low maintenance and no carbon emissions. Thermoelectrochemical cells utilise two electrodes, held at different temperatures, separated by an electrolyte containing a redox couple. The temperature dependence of the electrochemical redox potential results in a potential difference across the device. The magnitude of this temperature dependence is given by the Seebeck coefficient, S_e.

Until recently, research into thermoelectrochemical cells had primarily focused on aqueous media with the ferri/ferrocyanide redox couple. However, the good thermal and electrochemical stability, non-volatility and non-flammability of many ionic liquids makes them promising alternative electrolytes for these devices. Potential advantages include increased thermoelectrochemical device efficiencies, longer lifetimes and the ability to utilise waste heat in the 100 – 200 ^{o}C temperature range. There is also great scope for increasing the range of redox couples used for these devices.

Here we discuss our research into the use of different $Co^{(II/III)}$ redox couples in ionic liquids, and the influence of the ionic liquid on the temperature-dependant thermodynamics. We also discuss how different solvent/ionic liquid mixtures can yield significant improvements in power output.

ION-TRANSFER ELECTROCHEMISTRY AT ARRAYS OF NANOSCALE LIQUID-LIQUID INTERFACES

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Ion transfer electrochemistry across the interface between two immiscible electrolyte solutions (ITIES) offers a simple strategy to study chemical and biochemical sensing methods as well as transfers of relevance in biomembrane and industrial extraction processes. Sensing based on ion transfer electrochemistry relies on simple or facilitated transfer of ions, with sensitivity and selectivity achieved via the measured current and the applied potential of ion transfer, respectively. In order to improve the sensitivity of sensing based on electrochemistry at the ITIES, miniaturised (micro or nano) interfaces have been explored. Typically, single nanoITIES have been formed at the mouths of nanopipettes and applied to fundamental aspects of ion-transfer, e.g. kinetics. However, the low current signals and the delicate fabrication and handling procedures required have limited other applications of nanopipette-based ITIES. The preparation of arrays of nanoITIES within the nanopores of a perforated membrane enables an amplification of the electrochemical signal. Consequently, the current signal will depend on the array design, in particular the inter-pore spacing which should be optimised for independent mass transport to the interfaces located there.

In this report, the formation of nanoITIES arrays in silicon nitride membranes perforated with nanopores by focused ion-beam milling will be discussed. In particular the prototyping of nanopore arrays with different pore-pore spacings can be easily achieved, so that experimental and computational simulation studies of the mass transport effects at nanoITIES arrays can be undertaken. Direct comparison of experimental and simulated results will be presented and prospects for use in electrochemical sensing systems discussed.

IR825-Conjugated Polymeric Micelles for Fluorescence Imaging-Guided Photothermal Cancer Therapy

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Near-infrared (NIR) heptamethine cyanine dyes are ideal photothermal agents widely used in photothermal therapy (PTT). However, the clinical applications of NIR dyes are severely limited due to their poor water solubility, short circulation time, and low tumor-specificity. On the other hand, polyethylene glycol (PEG)-containing amphiphilic block copolymers are important drug carriers because of their good water solubility, "stealthy" property, and excellent drug loading capacity. Herein, a novel amphiphilic block copolymer was constructed by conjugating the hydrophobic NIR heptamethine cyanine dye, IR825-NH_2, to the double hydrophilic block copolymer, methoxypoly(ethylene glycol)$_{5K}$-*block*-poly(*L*-aspartic acid sodium salt)$_{10}$ (abbreviated as mPEG$_{5K}$-*b*-PLD$_{10}$) *via* the amine-carboxyl reaction. The as-prepared mPEG$_{5K}$-*b*-PLD$_{10}$-IR825 molecules can self-assemble into a polymeric nanomicelle (~25 nm) with PLD$_{10}$-IR825 moieties as the inner core and PEG$_{5K}$ segments as the outer shell. The nanomicelles possess high photothermal conversion efficiency, excellent water-dispersibility, high aqueous stability, superb tumor-specificity because of the enhanced permeability and retention effect, and low dark cytotoxicity. Furthermore, the covalent linkage between IR825-NH_2 and mPEG$_{5K}$-*b*-PLD$_{10}$ can effectively avoid the premature drug release during systemic circulation. *In vitro* experiments showed that the nanomicelles could be efficiently taken up by cancer cells and localize in the mitochondria and lysosomes of the cells. For *in vivo* experiments. after intravenous injection, these nanomicelles could efficiently target and completely ablate tumor under 808 nm laser irradiation, demonstrating their excellent PTT efficacy. We believe that the novel NIR photothermal agent developed in this work will hold great promise in nanomedicine.

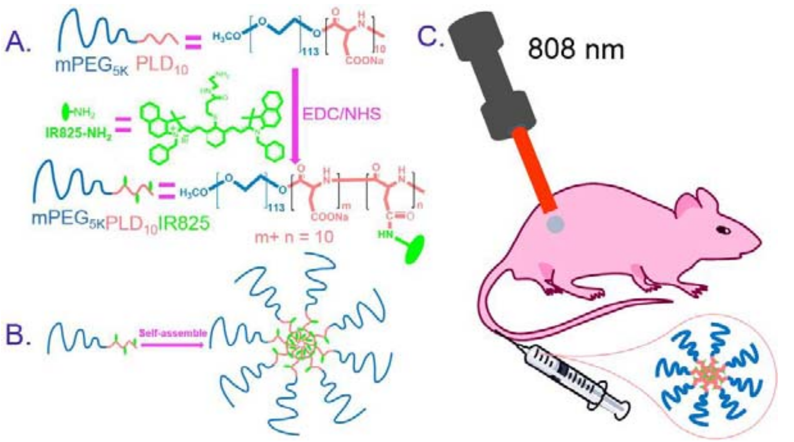

Fig. 1. Schematic illustration of mPEG$_{5K}$-*b*-PLD$_{10}$-IR825 micelle-based PTT.

Ira Remsen and the sweet bitterness of chemistry

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ABSTRACT

Ira Remsen was himself an important figure in the history of chemistry and in his later years gave many lectures on chemistry's history. He was born on 10th February, 1846 in New York City. He trained to be a doctor obtaining his MD in 1867. He followed the tradition of pursuing doctoral chemistry studies in Germany; he studied under Wilhelm Fittig at the University of Göttingen receiving a Ph.D. in 1870. He worked as a chemistry research assistant at the University of Tübingen for two years before returning to the USA as a chemistry professor at Williams College. He established a glowing reputation and was invited to become one of the original faculty of Johns Hopkins University. It was here that he turned the chemistry department into a chemistry research leader using the German model. This study will consider his writing, his founding of the *American Chemical Journal*, which he edited for 35 years and his pedagogy in assisting the beginner in chemistry. The story of the discovery of saccharin by himself and Constantin Fahlberg will retold as it is ironic that such a sweet substance caused such a bitter dispute. Remsen planned to come to Australia and New Zealand to attend the 1914 British Association for the Advancement of Science conference being held at various centres in Australia. The commencement of World War 1 prevented him reaching Australia. Remsen died on 4thMarch, 1927.

Iridium(III) Complexes as Efficient Photodynamic Therapy Agents via Protein Modifications

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ABSTRACT TEXT

Protein inactivation by reactive oxygen species (ROS) is considered to trigger cell death pathways associated with protein dysfunction; however, the detailed mechanisms and direct involvement in photodynamic therapy (PDT) have not been revealed. Thereby, we report herein Ir(III) complexes designed for ROS generation through a rational strategy to investigate protein modifications by ROS. The Ir(III) complexes were effective as PDT agents with low-energy irradiation because of the relatively high $^1O_2$ quantum yield, even with two-photon activation. In addition, two types of protein modifications (protein oxidation and photo-crosslinking) involved in PDT were characterized by mass spectrometry. Consequently, we present a plausible PDT modality that utilizes photo-activation of rationally designed Ir(III) complexes, indicating the feasibility of a better optimized Ir(III) complex for PDT.[1]

Furthermore, we report an Ir(III) complex, Ir-1, as a chemical tool for oxidation of amyloidogenic peptides which are related with Alzheimer's disease, upon photoactivation and subsequently modulation of their aggregation pathways. Our studies of Ir-1 demonstrate the next-generation of chemical tools for understanding their fundamental characteristics at a molecular level.[2]

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JAHN-TELLER SWITCHES BASED ON MIXED COPPER TUTTON'S SALTS

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ABSTRACT

Copper Tutton's Salts have the general structural formula $X_2[Cu(H_2O)_6](YO_4)_2$, where X is a mono-valent cation such as Rb^+, K^+, NH_4^+; and Y is S or Se. The crystals are all isomorphous, belonging to the monoclinic space group $P2_1/a$. The isolated $[Cu(H_2O)_6]^{2+}$ ions are on C_i symmetry sites with a tetragonally elongated octahedral geometry typical of six coordinate Cu(II) complexes.

The direction of the elongation axis varies depending on the identity of X and Y. The compounds $K_2[Cu(H_2O)_6](SO_4)_2$, $Rb_2[Cu(H_2O)_6](SO_4)_2$ and $Rb_2[Cu(H_2O)_6](SeO_4)_2$ all adopt a Form **A** with the long axis along the Cu-O(8) bond; while the compounds $K_2[Cu(H_2O)_6](SeO_4)_2$ and $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ both adopt Form **B** crystal with the long axis along Cu-O(7) bond.

We have investigated the mixed crystals of pairs of Tutton's salts that adopt the two different forms and have found a relatively sharp switch of the Jahn-Teller (JT) elongation axis as a function of composition. Near to this critical composition it becomes very easy to switch the JT direction by an external perturbation such as by changing the temperature. This behaviour can be modelled by considering the inherent Jahn-Teller activity of $[Cu(H_2O)_6]^{2+}$ ion embedded in the low symmetry environment of the lattice together with cooperative interactions between the JT ions that are mediate by the hydrogen bonding network. It becomes possible to predict favourable systems that can be easily switched and several of these will be presented.

KILLING GRAM-NEGATIVE SUPERBUGS WITH STAR-SHAPED PEPTIDE POLYMERS, NOT ANTIBIOTICS

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Antibiotic resistance in bacteria has reached alarming levels in many parts of the world, whereby common infections in some settings have become refractory to available treatment options. World Health Organization (WHO) has predicted that there will be 10 million people deaths each year due to drug resistant bacteria by 2050 if current trend continues. Essentially, we will enter a post antibiotic era, which will threaten the foundation of modern medicine. To avoid or delay these consequences, we need to restrict uses of antibiotics we currently have, encourage more research in the development of new antibiotics and think outside of the box and develop new alternative treatment methods. It was very encouraging to see a recent discovered new antibiotic which does not cause drug resistant.

In this presentation, we will describe a star shaped and peptide-based polymer which can kill Gram-negative bacteria as alternative medicine to antibiotics. The star was synthesized via a core-first and ring-opening polymerization of α-amino acid N-carboxyanhydrides. The *in* vitro tests have shown that bacteria's outer membrane is snapped away by stars and this gives one killing mechanisms. In vitro experiment has also demonstrated that the star does not cause any resistance by A. baumannii after 600 generation of the growth and in vivo model showed that the star can clear infection in mice by multi-drug resistant A. baumannii while the antibiotic, imipenem stopped working. A. baumannii has been recently classified as one of three Priority 1 pathogens by WHO.

Laboratory Studies of Trans-Neptunian Ices and Aerosols

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The recent New Horizons mission to the cold, outer edges of the Solar System has unveiled a library of small hydrocarbons and nitrile species generated by ultraviolet photolysis of nitrogen and methane. Within Pluto's atmosphere, abundances of C2-hydrocarbons reach supersaturation levels allowing the condensation of pure ices and aerosols – vehicles for higher-order products to the surface.

Generated by subsequent reactions with water ice, organics such as methanol, formaldehyde and acetic acid could provide a reservoir of biological precursors in the outer Solar System. Harboured on the cold surfaces of trans-Neptunian objects (TNOs) and comets, collisions may have delivered these materials to an early Earth.

However, the present-day detection of the icy grains of these minor constituents has been hampered by the opacity of hazy atmospheres and resolution limits of on board spectrometers and telescopes. Future missions operating in the far-infrared regions may overcome these issues to provide clearer spectra of crystalline ices where the composition and morphology of astrophysical surfaces can be ascertained.

We present our research into laboratory crystalline-phase molecular ices as analogues for pure ices deposited on TNO surfaces. Here, spectra are recorded between 20 and 180 K for vacuum deposited thin films grown with a new cryostat installed at the Far-Infrared/Terahertz Beamline at the Australian Synchrotron. Intermolecular lattice features are compiled and compared to periodic density functional theory (DFT) frequency calculations for the optimized molecular crystal structures. Prominent far-infrared features for the most abundant photoproducts and their composite water ice mixtures are detailed.

BIO-TUNABLE LIGHT ACTIVATED HYDROGEL *VIA* THIOLENE CLICK CHEMISTRY FOR 3D CELL CULTURES

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ABSTRACT

The complexities of the cellular environment are inherently overlooked when cells are cultured on a flat, two-dimensional (2D) surface. Recent advances have demonstrated that cells behave physiologically accurate when cultured in three-dimensional (3D) scaffolds.[1,2] Hydrogels have attracted large attention as a cell culturing scaffold due to their similar mechanical properties of soft tissues and ability to mimic native elements of the natural cell environment - the extracellular matrix (ECM).[1-4] The lack of controllability and reproducibility of current ECM scaffolds from natural materials such as collagen and fibrin, are key challenges that we are presently faced with.[2,4] The tunable and versatile nature of the synthetic hydrogels allows it to be controlled with the desired properties such as stiffness and porosity, also equipped with biological cues mimicking aspects of the ECM.[1,2,4]

Herein, our work describes the copolymerisation of poly(ethylene glycol) methyl ether acrylate and norbornene functional unit crosslinked with bisthiol-containing crosslinkers in the presence of a photoinitiator to form well-defined hydrogels under direct exposure to visible light. The polymers were synthesised *via* reversible addition-fragmentation chain transfer (RAFT) polymerisation enabling fine control over polymer length and molecular weight. Therefore, we are able to optimise the hydrogel stiffness and gelation time by varying the type of polymeric blend used, polymer length and the crosslinker concentration. Furthermore, the polymers were crosslinked with RGD cell adhesion peptide to investigate the ability of these hydrogel materials to support pancreatic cancer cells (p53^{R127H}). This provides a promising synthetic scaffold for culturing cells in a 3D environment.

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Liquid Metals as Sensors and Actuators

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ABSTRACT TEXT

Liquid metals such as Galinstan (70 % Ga, 20 % Sn and 10 % In) that are liquid at room temperature have received significant attention and have been investigated for many applications including soft electronics, repairable circuits, MEMS devices and plasmonics. The advantage of these materials is that they have high electrical conductivity, high density and extremely low vapour pressure. To broaden the applicability of liquid metals their surface chemistry can be manipulated via growth of an oxide layer or modification with semiconducting nanomaterials to generate photocatalytically active materials. Another area of interest is the controlled actuation of soft objects which has promise for many future environmental, biological or industrial processes.

In this work we describe how liquid metal galinstan can be electrochemically actuated in electrolytes of a wide pH range by application of an electric field. To improve performance we show that coating droplets of liquid galinstan with semiconducting nanomaterials significantly affects the velocity of liquid metal droplets. This concept is further developed by utilising galinstan as a liquid metal enabled pump in a closed-loop open-top channel whereby electrowetting/deelectrowetting at the surface of the liquid metal in a dynamic electric field induces a pumping action to give flow velocities of up to 5400 µL/min. Finally we show that the surface chemistry of liquid galinstan can be physically or chemically modified via immobilisation of nanomaterials, gallium leaching or galvanic replacement to create materials that can be used as electrochemical sensors for heavy metal ion detection or as heterogeneous catalysts.

LIQUID SALTS FOR CO_2 CAPTURE AND ELECTRO-CONVERSION

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Liquid salt is the collective term for both high temperature molten salt and room temperature ionic liquid [1]. Being ionic in nature, liquid salts can offer unusual ability for chemical and electrochemical reactions that are impossible in water and other conventional solvents. A good example is the use of liquid salts for capture and electro-conversion of the CO_2 gas. Several studies in early 1960s confirmed electrochemical reduction of the CO_3^{2-} ion to solid carbon in molten carbonate salts [2]. However, these findings did not attract immediate attentions, likely because cheap carbon can easily come from both fossil resources and biomass. Because the CO_3^{2-} ion can be formed by easy reaction of CO_2 with the O^{2-} ion (in the form of alkali or alkaline earth metal oxides), these early findings can form the basis for CO_2 capture and electrochemical conversion which has gained growing popularity recently [3]. On the other hand, variously functionalised ionic liquids are synthesised and used for CO_2 capture, whilst much less is reported on the reduction of the captured CO_2 in ionic liquids [4,5]. The author and co-workers have recently studied the feasibility of using liquid salts for capture and electrochemical conversion of CO_2 [3,6]. Results from these studies are summarised and discussed in this presentation, focusing on the advantages and disadvantages of molten salts and ionic liquids.

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LUMINESCENT ALKYNE-BEARING COMPLEXES, APPLICATION TO CHEMOSENSOR DESIGN AND PROTEIN LABELLING

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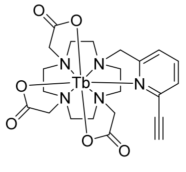
Our group is broadly interested in the development of luminescent lanthanide complexes for a range of applications. Here we describe the development of two "clickable" alkyne-bearing terbium complexes **1** and **2** (see below) that may be conjugated to azide-bearing molecules to introduce a luminescent moiety. We have applied these complexes to the development of a chemosensor for HS^- as well as the luminescent tagging of proteins.

The chemosensor, a bimetallic Tb(III)/Cu(II) complex (**3**), features **1** linked to a Cu(II)-DPA moiety. Detection of HS^- is based on copper sulfide precipitation, which produces a luminescent "switch-on" effect. The probe shows excellent selectivity towards HS^- over various anions and cations, displaying a 65-fold increase in luminescence in the presence of HS^-. The probe exhibits extremely fast reaction times and a low limit of detection (80 nM) and has been applied to the detection of HS^- in industrial "sour water".[1]

The utility of **1** and **2** for luminescent labelling of proteins has been demonstrated through conjugation to *E. coli* aspartate/glutamate-binding protein incorporating a genetically encoded *p*-azido-L-phenylalanine or *p*-(azidomethyl)-L-phenylalanine residue, introduced via stop codon reassignment technology. This tagging strategy may prove useful for developing time-gated LRET-based assays.[2]



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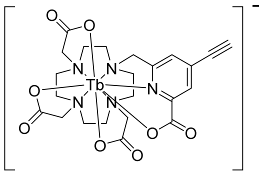

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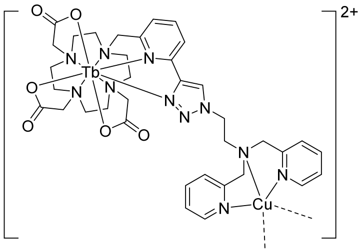

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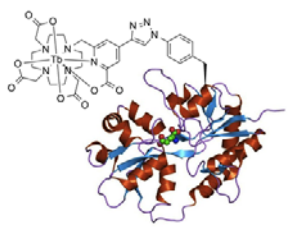

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LUMINESCENT RHENIUM(I), RUTHENIUM(II), AND IRIDIUM(III) COMPLEXES AS NOVEL CELLULAR REAGENTS

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ABSTRACT

The interactions of transition metal complexes with biological molecules have been of long-standing interest, and the applications of these complexes to modify biomolecules have been widely investigated. However, the use of luminescent transition metal complexes as intracellular sensors and bioimaging reagents has not been focused upon until recently. This interest is attributable to the high photostability, long-lived phosphorescence, and large Stokes' shifts of luminescent transition metal complexes. In particular, the interesting luminescence properties of rhenium(I), ruthenium(II), and iridium(III) polypyridine complexes have prompted us to develop new cellular reagents. We have modified these complexes with different functional groups and biological substrates to yield new biological labels and probes. These pendants include indole, estradiol, biotin, lipids, diaminoaromatics, alkynes, nitrones, poly(ethyleneimine), and poly(ethylene glycol). Remarkably, these units not only perturb the photophysical and photochemical properties of the complexes, but also significantly affect their biomolecular recognition and cellular uptake behavior. In this presentation, we will describe our design of these complexes to detect intracellular ions and small molecules; develop photofunctional cytotoxic agents; and label and image biomolecules from a bioorthogonal approach.

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Lung Cancer Diagnosis via Electrochemical Strategy: From miRNA to lncRNA

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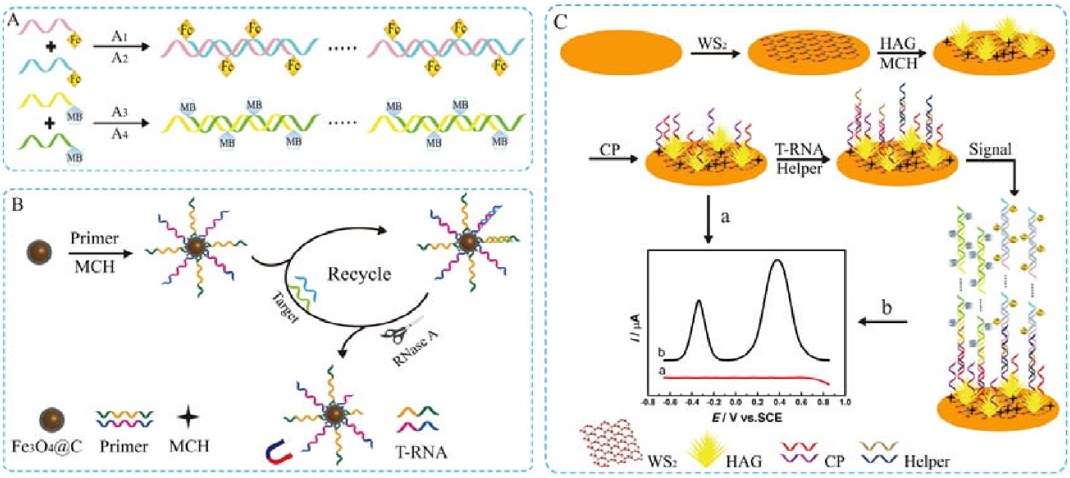
Lung cancer is a global health problem for its incidence, prevalence and high mortality rate. Therefore, sensitive and specific profiling of cancer-specific miRNAs or lncRNAs is significant. Until now, there are only a very few reports about lncRNAs detection using electrochemical biosensors. Therefore, the development of sensitive electrochemical detection of lncRNAs is highly desirable.

During these two years, we have fabricated three novel types of electrochemical genesensors for the detection of lung cancer related miRNAs and lncRNAs biomarkers. First, miR-21 levels were quantified as low as attomolar sensitivity by a target-triggered triple isothermal cascade amplification (3TICA) strategy with the coupling of target recycling, nicking-replication reaction and DNAzyme catalysis. Second, an H19 lncRNA electrochemical biosensor was fabricated based on a three-dimensional ordered macroporous (3DOM) graphene-AuNPs composite active interface and $Ru(NH_3)_6^{3+}$ attached AuNPs@PS signal reporter. Third, a multiplexed biosensor was prepared for the simultaneous detection of two different specific sequences deduced from MEG 3, on the basis of a 3D graphene-like WS_2 interface. In the presence of target specific sequence, an RNase A-aided target recycling amplification was triggered. Fc and (or) MB labelled chain reaction would subsequently generate signal enhancement, which was distinguished at different potentials. The application of these genesensors in real serum samples have also been studied, and the satisfactory results have already obtained compared with the clinical assays.



Scheme 1. Schematic illustration of multiplexed and amplified electrochemical detection of two different specific sequences deduced from MEG 3.

Material Degradation in High Temperature Molten Salts

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ABSTRACT TEXT

Using Phase Change Materials (PCMs) for solar thermal energy storage will require containers made from compatible materials. Corrosion of the container material will not only limit the lifetime of the containers but may affect the thermophysical properties of the PCM. This presents a materials challenge such as maintaining mechanical performance at high temperature >600 C, resistance to cyclic stresses and corrosion and having properties which will allow heat to be transferred. (Heat exchanger) Most previous materials work for solar thermal storage has been undertaken with lower temperature salts - i.e. Nitrates. The use of salts with higher melting temperatures and thermal cycling will magnify corrosion issues and an understanding of the mechanisms and factors which effect corrosion are needed for a proper engineering solution.

Materials development for polymer solar cells with efficiencies surpassing 10%

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Polymer solar cells (PSCs) have witnessed great progress with the research efforts from materials chemists and device physicists. Especially power conversion efficiency (PCE) over 12% has been achieved for bulk-heterojunction solar cells with the blend of polymer donors and non-fullerene acceptors. Donor-acceptor (D-A) type conjugated polymers with bandgap fine-tuned with intermolecular charge transfer are the mainstream of materials development. For most D-A polymers contributing championship efficiencies, benzo[1,2-b:4,5-b']dithiophene (BDT) and benzo[1,2-b:4,5-b']difuran (BDF) are the most widely used fused-ring donating units in constructing narrow bandgap polymers. Our group have developed facile synthetic approaches for 4,8-functionalized BDTs and BDFs with fine-tuned energy levels. Series of new polymer donors have been further explored for PSCs. In order to improve the performance of single layer PSC devices, two polymer donors with spectra-matching absorption have been solution-blended with acceptor to fabricate ternary solar cells, with PCE values over 10% readily achieved for the devices. The performance of PSCs is strongly dependent on the bandgap engineering of polymer donors, energy level matching between donors and acceptors energy levels, as well as the morphology tuning for the active layers.

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MEASUREMENT CHALLENGES FOR NANOMATERIALS

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ABSTRACT TEXT

As nanotechnology matures and products containing nanomaterials become routinely available, engineered nanomaterials are increasingly likely to enter the environment through direct application (e.g. fertilizers or site remediation), product degradation and disposal (e.g. paints, coatings and personal care products), and waste streams (e.g. washing of smart fabrics, foods and nanomedicines). Accurate detection, quantification and characterisation of nanomaterials is required to monitor their distribution in the environment and inform safety guidelines for use, disposal, and remediation.

Particle size distribution (PSD) is widely recognised as one of the key characterisation parameters, along with the number and/or mass concentration, chemical composition, agglomeration/aggregation state, surface charge and surface chemistry. While a diverse range of methods for characterising PSD exists, they all have inherent biases, strengths and limitations.

Here we present an overview of some of the available particle size characterisation techniques (dynamic light scattering, particle tracking analysis, atomic force microscopy, transmission electron microscopy, differential centrifugal sedimentation, and asymmetric flow-field and sedimentation-field flow fractionation) and briefly discuss some of the benefits and limitations associated with each of them. We use an example of measurements made on citrate stabilised Au colloids; as monomodal suspensions and multimodal mixes which allow us to better understand instrument performance and to address issues that are related to determining measurement uncertainties on the nanoscale.

The results of this study clearly illustrate the advantages, limitations and biases of different measurement techniques and are useful for scientists and researchers who perform and interpret size measurements on nanoscale particle systems.

Measurements of radicals in the atmosphere and comparison with models

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The OH radical removes the majority of trace gases in the atmosphere emitted either naturally or via human activities, initiating the formation of a wide range of secondary products, many of which are implicated in poor air quality, for example ozone and organic aerosols. However, *in situ* measurements of OH and other radical species in the atmosphere are extremely challenging, and laser-induced fluorescence (LIF) spectroscopy offers a very sensitive method for their quantitative detection. The presentation will describe LIF detection of atmospheric OH, HO_2 and RO_2 radicals (with some limited speciation) at low pressure using the so called FAGE (fluorescence assay by gas expansion) technique from ground and airborne platforms. Laser-based measurements will also be described of formaldehyde, glyoxal and OH reactivity, the latter being a kinetic parameter representing the total removal rate of OH via reaction with its atmospheric sinks. The specific detection of CH_3O_2 radicals will also be described via a new method. Comparison of field measurements of radicals and other short-lived species with numerical model calculations constitutes one of the best ways to evaluate chemical mechanisms within models. The detailed *Master Chemical Mechanism* is used which contains up to ca. 6,700 chemical species and 17,000 reactions. The presentation will show examples of measurements and model comparisons from field campaigns in a range of environments, including the remote marine boundary layer, a tropical rainforest and the mega-cities of London and Beijing. The impact of some new laboratory kinetic and photochemical data on atmospheric composition will also be discussed.

Measuring macromolecular crowding in cells through fluorescence anisotropy imaging with an AIE fluorogen

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Macromolecular crowding effect is ubiquitously occurring in almost all types of cell and influences such processes as protein diffusion, folding, association, aggregation and so on. Direct visualisation of the crowding effect with spatiotemporal resolution would be desirable to determine the impact of excluded volume on the biological processes in cells. I will present a simple and general approach we design based on fluorescence anisotropy imaging with an aggregation-induced emission (AIE) fluorogen to measure the crowding effect in the heterogeneous and dynamic cellular milieu. The utilization of the AIE dye for investigating the intracellular environment will also be introduced.

Mechanism and Control of the Selective Fragmentation of Protein Ions

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Whole protein mass spectrometry (MS) is an emerging approach in which intact protein ions can be isolated and fragmented without proteolytic digestion. The primary advantage of intact protein MS is that degradation products, sequence variants, and different combinations of post-translational modifications can be distinguished. However, a key challenge is that ion fragmentation methods generally result in non-specific dissociation, which can significantly limit protein identification because ion signal is diluted between hundreds of fragment ions.

We have discovered that protein ions in very high charge states (CSs) dissociate selectively in higher-energy collision-induced dissociation (HCD). As CS increases, the extent of fragmentation and sequence coverage decreases significantly. This is attributable to predominantly non-specific cleavages at lower CSs while selective fragmentation is observed at higher CSs. By comparing measured cleavage sites to calculated protonation sites, these data indicate that "mobile" protons drive fragmentation. At lower CSs, where basic sites are protonated, additional collision energy is required to mobilize protons onto backbone sites for fragmentation. At sufficiently high CSs, protons are localized on backbone residues prior to HCD. Thus, highly selective fragmentation occurs near the predicted sites of backbone protonation.

Our results indicate that low CSs are desirable for obtaining extensive sequence information for deep sequence characterization. Alternatively, HCD of high CSs can result in the formation of selective sequence ions, which can be used as "sequence tags" for protein identification. Now, the "optimal" CSs of protein ions can be predicted to enable selective and controlled dissociation for generating sequence tags with maximum sensitivity.

Mechanisms for Combating Fungal Biofilm Formation on Biomaterial Surfaces

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Polymicrobial biofilms can be formed on surfaces by microbial colonisation of materials such as biomedical implant devices and also can be caused by bacterial or fungal species, or both kinds of microbes. In the last two decades, research has mostly been focused on bacterial infections and anti-bacterial surfaces. Although fungal infections related to biomaterials are increasing and threatening human lives, the number of studies are still very low and have received comparatively little interest. Attachment of fungal cells onto biomaterial surfaces is the first step for biofilm formation. Hence, this initial attachment should be prevented, which can be done with two different strategies.

One strategy to combat fungal biofilms is preparing coatings with covalently bound FDA-approved antifungal agents such as echinocandins and polyenes on the biomaterial surfaces, for long-lasting effects of antifungal compounds with sufficient concentration on the appropriate site of surfaces in contact with fungal cells. Using surface-activating plasmas or plasma polymer interlayers such as propionaldehyde, ethanol and propionic acid plasma polymers with desired surface chemical groups is an appropriate and straightforward method to graft bioactive molecules on various solid surfaces.

A second strategy is to encapsulate and release low molecular weight antifungal molecules such as azoles. Loading fluconazole, from the approved class of azoles which are able to target cell membranes and intracellular parts of fungal cells, offers an avenue for creating coatings that can selectively deter fungal colonization while supporting mammalian cell attachment. As a carrier coating for releasing the drug, heptylamine plasma polymer is a good option for its simple deposition technique, good absorption of drug, and compatibility with innate immune cell function. Results of characterization, analysis and biological assays will be discussed.

METAL CLUSTERS IN PHOTOCATALYSIS

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We are exploring the use of atomically-precise, chemically-synthesised metal nanoclusters deposited on various forms of titania (TiO_2) with a view to measuring and understanding their role as co-catalysts in photocatalytic systems. Although measurement of their catalytic activity is important, it is vital to identify and understand the geometric and electronic structure of the chemically-equivalent active sites to make further gains in photocatalytic efficiency and efficacy. Theoretical modelling can be used to provide insight to interpret and explain experimental analysis and observation. This is particularly advantageous since the exact composition of a cluster ameliorates any size approximation, thus affording the potential to explore size-effects from a theoretical perspective.

This presentation will describe our characterisation of several metal cluster systems including synchrotron-based Far-IR and X-ray Photoelectron Spectroscopies (XPS), Metastable Helium Induced Electron Spectroscopy (MIES), as well as Atomic Force Microscopy (AFM) and Scanning Transmission Electron Microscopy (STEM).[1-9] We use density functional theory to calculate properties of the initial metal cluster as well as the interaction between cluster and TiO_2 semiconductor substrate. The calculations provide density of states (DOS) information to assist with analysis of the MIES and XPS data. Crucial to the comparison of calculated versus experimental properties is the benchmarking procedures that we have developed. We are also developing Density Functional Tight-Binding (DFTB) parameters to allow rapid geometry optimisation of large, chemically-relevant systems.

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Metal Microcapsules For Actively Triggered Localised Drug Delivery

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Until recently, small, volatile actives could not be efficiently encapsulated for timescales longer than a few days, due to the inherent porosity of the polymeric membranes used as the capsule shell material. Using electroless deposition of metals, we have developed a method for preventing undesired loss of encapsulated actives.[1]
Polymer microcapsules are produced using solvent evaporation to precipitate a polymeric shell around an oil core.[2, 3] Metal nanoparticles on the polymeric shells are used to catalyse the growth of a secondary metallic shell.[4] This shell prevents core loss for >30 days, as opposed to polymeric capsules which lose their entire core in less than 30 minutes under the same conditions.
One exciting application of these metal microcapsules could improve the prognosis of patients with high grade glioma, providing an alternative, more effective treatment to those currently available. Typical treatment of brain tumours involves surgical removal of the majority of the tumour, followed by radiotherapy and chemotherapy. Unfortunately, recurrence is common, often resulting in patient mortality.

The localised delivery of chemotherapy drugs using biodegradable wafers implanted into the resection cavity has demonstrated a modest improvement in survival in patients with both recurrent and newly-diagnosed glioma.

A significant improvement to this approach could be gained by actively triggering drug release at the site of tumour recurrence. We have made considerable progress in the development of metal-shell microcapsules as responsive drug-delivery vehicles. In this way, we can deliver high doses of drug to recurrent tumours in a highly localised, controlled and non-invasive fashion.

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Metal-organic frameworks derived nanostructures for energy storage and conversion

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ABSTRACT TEXT

Developing energy storage and conversion devices with high efficiency, low cost and environmental benignity is of great significance in addressing the problems of increasingly worsening environmental pollution and the impending exhaustion of fossils. Here, we developed a series of functional metal-organic frameworks (MOFs)-derived nanostructures for energy storage and conversion by controlling heat treatment. Through a two-step heat treatment, we adopted a facile interface-modulated method to synthesize yolk-shell carbon-based Co_3O_4 dodecahedrons which exhibited excellent lithium and sodium storage. Moreover, by a low-temperature (as low as 430 °C) pyrolysis process, a facile, general and high-yield strategy was also developed for the oriented self-assembly of carbon nanotubes (CNTs) from selected MOFs. This method was then successfully extended to obtain a variety of oriented CNT-assembled architectures by modulating the corresponding MOFs, which further homogeneously incorporate heteroatoms into the CNTs. Specifically, nitrogen-doped CNT-assembled hollow structures exhibit excellent performances in oxygen reduction reaction. On the basis of experimental analysis and density functional theory simulations, these superior performances are attributed to synergistic effects between ideal components and multilevel structures. In addition, the appropriate graphitic N doping and the confined metal nanoparticles in CNTs both increase the densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. These MOFs- derived nanostructures will hold great potential in many frontier fields.

METHODS FOR INVESTIGATING AUSTRALIA'S FORMER NUCLEAR TEST SITES

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The radiological residues at the former weapons testing sites in Australia at Maralinga, Emu and the Montebello Islands are of ongoing interest in terms of environmental fate, transport, and uptake into the biosphere[1]. The physical and chemical characteristics of these residues affect their mobility and availability for uptake into living organisms[2]. At the Taranaki site, Maralinga, substantial body burdens of Pu were observed in mammals, likely due to the presence of respirable particles. Actinides often occur in particulate forms that, for characterisation, require advanced techniques including Accelerator Mass Spectrometry (AMS)[3], scanning electron microscopy and synchrotron X-ray fluorescence microscopy (XFM). Many nuclear test site particles have core-shell, or inhomogenous structures where the surface is dominated by lighter elements sourced from local soils and the Pu concentrated in the interior[4]. Modelling results suggest that for respirable-sized Pu-containing particles (that can be inhaled and lodged in the lung), most of the alpha emissions escape the particle and are deposited in the surrounding tissue.[5] For larger particles, (e.g. >7 µm), which typically do not lodge in the lung but could be ingested, most of the alpha emissions do not escape the particle, but are instead captured within the particle itself (self-shielding) therefore decreasing the effective dose. We are currently using advanced techniques to compare the radionuclide forms from the inland sites (Maralinga and Emu) with the marine site (Montebello Islands).

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METHODS TO ACCESS SMALL, MEDIUM AND LARGE HETEROCYCLES

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Most of the time, the synthesis of complex biologically active molecules are problematic but, the problems encountered during the syntheses, can be a good source of inspiration to develop methods. One major challenge is the design of concise strategies as well as chemoselective and efficient methods that rapidly lead to the skeleton framework of natural and/or biologically active heterocyclic compounds.

In this context, we have explored the construction of heterocycles using catalytic reactions involving transition metal catalysts. Transition metal catalysts can induce rearrangements, cyclizations, functionalizations which can be highly diastereoselective and enantioselective if a chiral ligand is added in the reaction media. These reactions and their applications to the synthesis of heterocyclic natural and non-natural products will be presented.

Microfluidic Approaches to Studying Mineral Processing Phenomena

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Microfluidic devices offer promising platforms to study mineral processing phenomena, from leaching to phase transitions (e.g. crystal growth) to phase transfer (e.g. solvent extraction). Microscale interrogation of these processes permits new insights into crucial physicochemical phenomena and, we argue, provides knowledge that can be applied to bulk-scale processing.

Here, open ("pillar cuvettes") and closed (channels in glass) microfluidic devices are used to investigate leaching of gold in micro and nano-scale channels (analogous to cracks and interstitial spaces in heap leaching). Leaching progress follows diffusion-limited rates and the sensitivity to leach solution stoichiometry (thiosulphate solutions) is readily obtained. Further, solvent extraction rates for platinum and rare earth elements (REEs) and the early stages of third phase formation are investigated. Extraction of Pt and REEs was shown to be faster in the microfluidic chips due, in part, to the higher surface/volume ratios involved and can be tracked in real-time using micro-spectrophotometry. For third phase formation, we show that extraction of ytterbium at high concentrations (15-20 g/L) using 33% Cyanex 572 leads to nucleation of third phase on glass surfaces treated with a hydrophobic self-assembled monolayer (using silane chemistry), in preference to hydrophilic (clean) glass.

These observations will be discussed in terms of mineral processing scenarios encountered in industry and, for solvent extraction, the opportunity to scale-out microfluidic modules for throughput scale-up.

Microfluidic Fabrication of Calcium-based Biomaterials to Promote Patient Specific Osteogenesis

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Orthopaedic intervention requires the replacement of native bone with graft material in a wide range of clinical scenarios. As a result, there is significant demand for biomaterials capable of improving bone healing, whilst reducing the rate of postoperative adverse outcomes. Currently, the production of synthetic bone graft materials requires sintering, acidic conditions, and extensive purification prohibiting the incorporation of temperature sensitive molecules during synthesis. Using the Vortex Fluidic Device (VFD) we have developed a scalable continuous flow-processing regime capable of producing calcium based cellular scaffolds at room temperature (**Fig 1a**). Vortex Produced Calcium Matrices (VPCM) contain crystalline domains and calcium phosphate ratios similar to that of native bone. The production of VPCM occurs at room temperature under conditions that allow the incorporation of temperature sensitive protein growth factors and pharmaceuticals during synthesis (Yuan et al., 2015). Thus VPCM may be used as a base material where the incorporation of bioactive molecules allows the matrix to be tailored to clinical need. As a proof of concept, we have demonstrated that it is possible to incorporate Bovine Serum Albumin within VPCM (**Fig 1b**). Furthermore, to investigate the role of VPCM as a drug delivery vehicle we have shown that it is possible to incorporate Doxycycline, a tetracycline antibiotic with osteogenic properties, within VPCM during its synthesis (**Fig 1c**). These experiments demonstrate the utility of the VFD in the production of versatile calcium based matrices that maybe tailored to clinical need through the incorporation of specific bioactive agents during synthesis.

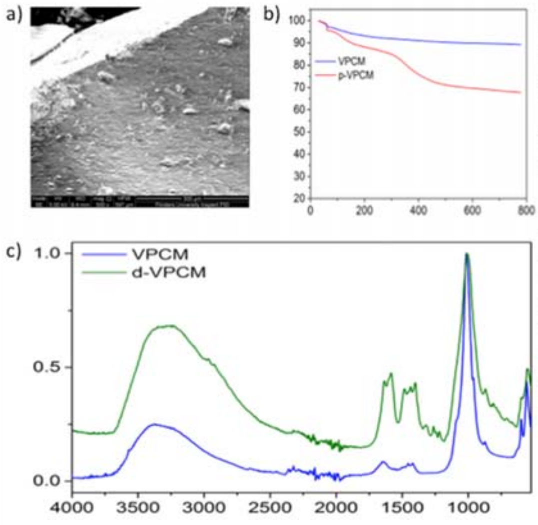

Fig. 1 a) SEM of VPCM produced using a 20 mm diameter VFD tube. **b)** Thermogravametric analysis of protein loaded VPCM (p-VPCM) where Δ weight ≈ 30%. **c)** Infrared absorbance of doxycycline loaded VPCM (d-VPCM) (green) compared to VPCM absorbance (blue) indicating doxycycline inclusion within VPCM.

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MIKTOARM STAR POLYMERS FOR DRUG DELIVERY BY RAFT POLYMERISATION

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ABSTRACT

Brain cancers such as glioblastoma multiforme are some of the most dangerous cancers with an alarmingly high mortality rate. It is reported to have the lowest survival rates at less than 20% survival rate over 5 years. There are many reasons for this but a major one is the ineffective delivery of anticancer drugs to the tumour location. This is due to the presence of certain barriers in the brain (for example, the blood brain barrier, BBB), which protect the brain from harmful materials and also restrict the entry of useful therapeutic molecules.

The present project deals with a non-invasive approach, involving the synthesis and evaluation of a range of cross-linked mikto-arm star polymers as candidates for the delivery of anticancer therapeutics across the BBB. The synthesis will be undertaken by the Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation process.

Narrow dispersity, hydrophobic poly (butyl methacrylate) and hydrophilic poly (PEG methacrylate) arm polymers with different chain lengths and were synthesised via RAFT. These were reacted with a dimethacrylate to give core cross-linked miktoarm star polymers with particle sizes ranging from 120-300 nm. A monomeric conjugate of antineoplastic drug SN38 was synthesised independently to incorporate into the structure during cross-linking. This presentation will highlight the synthetic approach to a range of star polymer conjugates and will explore structure-property relationships such as hydrophobicity/hydrophilicity- cross link density, and drug loading. An *in vitro* evaluation of the efficacy of these mikto-arm polymers to cross a BBB model system will be reported.

Mobile Devices as Scientific Instrumentation

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The rapid expansion of mobile phones and other mobile technologies is set to transform biochemical and chemical sensing landscape. In particular the widespread availability of smartphone technology and the capabilities they offer in terms of computation, communication, networking, and imaging will allow a more extensive deployment of lab-on-a-chip and related sensing technologies. Furthermore the combination of mobile technologies with low-cost sensing concepts such as paper microfluidics could make life-changing health and environmental testing technologies available to many millions more people both in the developed and developing worlds.

Voltammetry is the cornerstone technique of electrochemical sensing, and almost all dynamic electrochemical methods can be regarded as a variation of the basic voltammetric method. The ability to provide not only sensitive quantitative information from the magnitude of the current peak, but also a degree of selectivity offered by the potential axis of the voltammogram, is the reason voltammetric methods have enjoyed such enduring popularity. In one example, we will show that quantitative voltammetric analysis may be carried out using only the intrinsic hardware in a mobile device such as a phone or tablet, with the aid of a suitable software application, using no external device or instrument whatsoever. We call this new approach Android voltammetry.

MODELING SURFACE MOTION IN GAS-SURFACE SYSTEMS

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ABSTRACT

In the last decades, dynamics calculations based on physically accurate models have become an important tool used to obtain a better understanding of gas-surface experiments. As a result of this close collaboration between theory and experiment, it has become clear that theoretical models need to treat correctly, at least, all the significant degrees of freedom (DOFs) of the chemical process of interest. This usually means that all the molecular projectile DOFs have to be included in the model. However, surface DOFs have proven to play also a major role in the dynamics of such systems, as they allow surface atoms to move from their equilibrium positions, they allow energy exchange between the projectile and the surface, and they may change reaction barrier shapes and location.

One of the successful algorithms developed in the recent years to model gas-surface reactions, is the Grow [1] procedure in conjunction with the symmetry adapted modified Shepard interpolation method [2]. So far, this algorithm has been implemented to treat either gas-static surface systems, or dynamic surfaces that are not interacting with any adsorbate. However, in this work we have extended the current implementation to deal with the case of a dynamic surface interacting with a molecular projectile. To test the new implementation, we have built a PES based on an analytical many-body model potential. We have designed this potential to qualitatively reproduce the behaviour of reaction barriers when surface atoms are in motion, as proposed in recent theoretical studies [3].

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Modular synthesis and photocontrollable biological activity of carbohydrate-based amphiphiles

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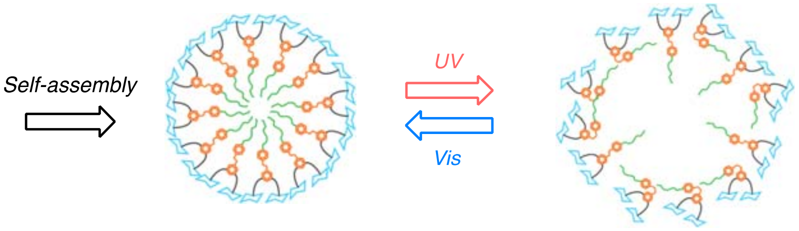
Amphiphilic carbohydrates play essential roles in biology as structural motifs for membrane support and function, and as mediators for cellular communication.[1] These molecules are also of major industrial importance given their applications as detergents, wetting agents and emulsifiers.[2] The self-assembly of naturally occurring and synthetic carbohydrate-based amphiphiles in water is well-documented and gives rise to micellar structures with diverse morphologies and useful properties.[3] The ability to control the interfacial activity and self-assembly properties of glycoamphiphiles with an external stimuli provides exciting opportunities for controlling biomolecular recognition processes, and the development of vehicles for triggered release applications in organic synthesis, bio- and nanotechnology, and biomedical research.[4] In the following presentation, we discuss the modular synthesis, photocontrollable interfacial activity and self-assembly properties of carbohydrate-based amphiphiles, including surfactants, $\pi-\pi$ self-assemblies and cluster glycosides (dendrons) (Figure 1).[5,6] We will also highlight the photocontrollable biological activity of these amphiphiles as potential light-addressable cryoprotectants[7] and bacterial biofilm inhibitors.[8]



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MODULATION OF ALTERNATIVE SPLICING USING SMALL MOLECULES: TOWARDS THE TOPICAL TREATMENT OF NEOVASCULAR EYE DISEASE

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The splicing of pre-mRNA is one of the main processes that influences protein diversity in humans and recent studies have estimated that up to 88% of multi-exon protein coding genes are alternatively spliced. This diversity highlights the importance that alternative splicing plays in regulatory affairs, such as cell growth, differentiation and apoptosis. Alternative splicing is carried out by cellular machinery known as the spliceosome and this machinery is regulated by the phosphorylation of key splicing factors. By controlling the phosphorylation events, it is possible to regulate the production of protein isoforms.

To achieve this, we have been developing inhibitors of the kinases (such as SRPK1 and the Clks) responsible for the phosphorylation events. This talk will describe the development of new scaffolds that have resulted in the generation of inhibitors that are able to inhibit the kinases with single digit nanomolar IC50s.

Data will be presented that demonstrates how some of these inhibitors can be used to regulate the alternative splicing of VEGFA, one of the critical proteins involved in angiogenesis. These inhibitors represent the first steps in the development of a potential topical therapeutic for the treatment of neovascular eye disease.

MOFs@SiO$_2$ PARTICLES AS STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

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ABSTRACT TEXT

Metal-organic frameworks (MOFs) are highly ordered crystalline materials that are formed by linking metal-containing units with organic linkers through the use of coordination bonds. Since their invention, these materials have received considerable attention due to the flexibility with which they can be prepared, their tunable porosity as well as the possibility for chemical functionalisation. Owing to these properties, MOFs have been recently applied in the field of separation science as stationary phases for HPLC_ENREF_1_ENREF_1.

In this work the synthesis of MOFs@SiO$_2$ particles will be presented. The hybrid particles exhibited an unusual flow-dependent separation selectivity (FDSS) of small molecules as a result of the well-defined microporous structure of the MOF shell. The FDSS effect allows changes of both the retention and separation selectivity of small molecules by simple variation of the mobile phase flow rate under isocratic conditions.

The prepared particles were also tested for the normal-phase (NP) and reversed-phase (RP) separation of xylene isomers, substituted benzenes and polyaromatic hydrocarbons (PAHs) achieving efficiencies that exceed the best values reported in the literature using MOFs as stationary phases in LC. Thus, the data to be presented will show the potential of MOFs as new separation media for the efficient separation of closely related compounds (e.g. positional isomers).

MOF-Templating Route for Synthesising Efficient CO2 Methanation Catalyst

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Methane is a promising chemical for future energy storage. Through the Sabatier reaction, renewable methane can be synthesised from CO_2 and renewable H_2. Although H_2 itself can be used for energy storage, CH_4 presents advantages regarding storage, transportation and safety. The advantages of using methane over H_2 as an energy carrier have been acknowledged by several space programs which are currently developing new engine technologies to replace H_2 by methane. On Earth, CH_4 from fossil sources has many applications and renewable CH_4 can accommodate the current technology while using a sustainable source. In this work, we investigated new catalysts for the CO_2 methanation. This presentation will showcase the discovery of a new synthesis route for very active Ru/ZrO_2 catalysts. A highthroughput (HT) approach was used initially to screen more than 100 different materials. Next, the best performing catalyst was assessed at different reaction conditions and alongside a number of controls, at all conditions, the catalyst displayed remarkable activity. Samples with the same chemical composition were synthesised via different routes but underperformed as catalysts, this indicated that the high activity of this catalyst can be related to the structure of the final catalyst. This efficient catalyst was synthesised under Sabatier reaction conditions using a Zrbased metal-organic framework template impregnated with Ru. The resulting catalyst structure was carefully investigated using a wide range of techniques and indicated the presence of hexagonal Ru^0 nanoparticles highly dispersed on nanoZrO_2

Molecular Dynamics Study of Partitioning of Hydrophilic Monomers in Aqueous Solution

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The application of pulsed-laser polymerization size-exclusion chromatography (PLP-SEC) has made it possible to unambiguously determine propagation rate coefficients (k_p) in radical polymerization in a single experiment. Accurate Arrhenius parameters are now available for a wide range of monomers, where previously great uncertainty prevailed even for very common commodity monomers. While propagation rate coefficients are largely insensitive to solvent effects and to monomer concentration, water is a significant exception for many monomers. The currently accepted model attributes changes in k_p to a decrease in the Arrhenius pre-exponential factor when water is replaced with monomer in the environment of the transition state, reducing degrees of rotational freedom[1], but this is problematic in terms of statistical thermodynamics.

We hypothesise that partitioning arises for these monomers due to the robust ice-like structure of liquid water and that, prior to the total disruption of the water structure by dissolved monomer, aqueous solutions are effectively heterogeneous on the propagation timescale with polymer and monomer excluded from regions where water displays medium range order, and restricted to regions of disordered water exhibiting a much higher effective concentration for polymerisation. We are utilizing molecular dynamics simulations to study the extent of water structure disruption and the extent of clustering of monomer molecules in water/monomer mixtures in order to determine if the trends obtained are consistent with experimental observations.

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Molecular Engineering of Drug Therapies and Diagnostic Platforms

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ABSTRACT TEXT

Biologic drug therapies based on proteins, RNA, DNA and engineered cells have the broad target range that could translate the potential of the Genome Era into impactful new classes of therapeutics and Individualized Medicines. Today, however, biologic drug therapies are often limited by delivery and manufacturing barriers. We have been developing polymeric drug carriers and cell manufacturing systems that enable new approaches to biologic therapies. These platforms also provide opportunities for small molecule therapies and biomarker/diagnostic profiling. The delivery systems for proteins and nucleic acids mimic the highly efficient intracellular delivery systems found in pathogenic viruses and organisms. The carriers are applicable to a wide range of biotherapeutics, and might open up new families of peptide, antibody or nucleic acid drug candidates that attack previously inaccessible intracellular targets. Polymeric materials of a similar class are being developed to improve biomarker and cell isolation technologies, as well as to improve biological manipulation steps necessary to scale and streamline new T-cell and stem cell therapies. This talk will highlight some of the new capabilities of the therapeutic, diagnostic, and cell manufacturing platforms.

Monolith for Miniaturised Plasma separation

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Many point of care testing (POCT) platform utilises plasma to perform analysis on various target analytes without the interference of red blood cells and the use of simple optical detection. Plasma are generally separated from whole blood via the conventional method of centrifugation, a technique that is difficult to automate and is even more challenging to implement with very small blood volumes. Herein, lies a need for an improved method of plasma separation from whole blood that only requires microlitre volumes of whole blood and results in an optimal amount of plasma. Porous polymer monoliths are a single piece of material that does not contain interparticular voids, which significantly reduces the void volume making the monolith an extremely useful separation matrix in the field of separation science, especially for microliter volumes. In this undertaking we demonstrate the use of a porous polymeric monolithic device for the separation of plasma from whole blood. The main constituents of the photo-polymerized monoliths involved are monomer: 2-hydroxyethyl methacrylate (HEMA), cross-linker: ethylene glycol dimethacrylate (EDGMA), photo initiator and porogens. The aim of this study is to validate the usage of monoliths as a separation device compared to the conventional method of centrifugation. The viability of integrating the monolith into a microfluidic system to enable the development of aa standalone POC testing device will be discussed. Such a device would be applicable in a low-resource setting and therefore have features that make it affordable, sensitive, specific, user-friendly, rapid, robust, equipment-free, environmental friendly and accessible to the to the end user.

Multifunctional Electrocatalysts and Application in Energy Conversion and Storage

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ABSTRACT : The growing problems associated with energy security and environmental pollution have stimulated extensive efforts worldwide to the development of green and renewable energy technologies, including, metal−air batteries, fuel cells, electrolysis cells, and solar synthetic reactors.[1-3] Hydrogen evolution reaction (HER), Hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), oxygen evolution reaction (OER) are the most crucial electrochemical processes and usually coexist to realize energy storage and conversion in these technologies. Typical examples are the metal-air battery involving ORR and OER, and the water splitting process combining HER and OER. Development of multifunctional electrocatalysts with low overpotentials and high activities is a crucial thought for simplifying the design of the electrocatalytic electrodes for fuel cells, metal−air batteries and overall water splitting setup.[4,5] herein ,we will report some multifunctional electrocatatlysts and their application in the energy conversion and storage.1, robust trifunctional electrocatalysis by Co/CoxOy/CoNC coupled N-doped graphene hybrids for zinc–air batteries and self-powered water splitting, 2, a photo-responsive bifunctional electrocatalyst for oxygen reduction and evolution reactions.

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Velocity-map imaging the UV photodissociation + VUV dissociative ionisation of 2-bromothiophene

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The velocity-map imaging (VMI) apparatus at Bristol has been recently extended to incorporate a PImMS2 camera[1] for multi-mass imaging and a vacuum ultraviolet (VUV) laser source for 'universal' detection, allowing more holistic insight into rich photochemistry. This talk will provide a brief overview of these experimental enhancements before discussing the results of a study into the ultraviolet (UV) photochemistry of 2-bromothiophene (C_4H_3SBr).[2] This molecule has been studied previously by velocity-map imaging the Br fragment, revealing striking wavelength-dependent photophysical behaviour and providing some evidence for gas-phase photochemical ring-opening.[3] In this work, multi-mass imaging and universal detection were used to simultaneously observe the thiophenyl fragment and any other lighter masses formed.

The UV photodissociation of 2-bromothiophene was investigated across the photolysis wavelength range $265 \geq \lambda_{phot} \geq 245$ nm with ionic fragments detected following VUV ionisation with 118 nm light:

$$C_4H_3SBr \xrightarrow{\lambda_{phot}} C_4H_3S + Br$$

$$C_4H_3S \xrightarrow{\lambda_{118nm}} C_4H_3S^+ + C_3H_3^+ + CS^+ + HCCS^+$$

At all wavelengths, the Br-loss photoproduct (C_4H_3S) was found to exhibit recoil velocities and anisotropies consistent with those reported elsewhere for the Br fragment.[3] Velocity-map images for all lighter ions were also acquired simultaneously and include a $C_3H_3^+$ channel that dominates the ion yield spectrum at $\lambda_{phot} \leq 255$ nm. Anisotropy and velocity information from these images, alongside those from the REMPI-ionised Br fragment, reveal that these lighter ions arise from dissociative ionisation (from the VUV probe laser) of the most internally excited C_4H_3S fragments.

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MULTI-RESIDUE ANALYSIS WITH ADVANCED SEPARATIONS: PESTICIDES, PETROCHEMICALS, AND PHOSPHATE ESTERS

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The flame photometric detector (FPD) provides sensitive and specific detection for sulfur (S) and phosphorus (P) in organic compounds. The analysis of organo-S and -P compounds is important in a range of samples, such as pesticides (e.g. both S and P in phosphorothioates), petrochemicals (e.g. S in thiophenes, benzothiophenes and dibenzothiophenes), and phosphate esters (e.g. P in flame retardants, and chemical weapon degradation products). Comprehensive two-dimensional gas chromatography (GC×GC) provides excellent separation capabilities for multi-residue samples, and combined with the specific FPD detector permits overlapping matrix removal, and useful speciation in the 2D separation. We have shown that the FPD(S) mode suffers from some detector-based tailing, reducing its utility as a detector for very fast GC×GC peaks, but the FPD(P) mode demonstrates classic GC×GC peak shapes, high resolution, and excellent detection limits at ppb levels. GC×GC-FPD was used to study pesticides in vegetables, to compare detector performance across a range of detection methods (ECD, FPD(P), FPD(S), NPD and TOFMS), for S-rich shale oils and fuels, and for a multi-component pesticide/phosphate ester mix in a 5% diesel matrix as a demonstration of potential performance relevant to chemical weapons degradation. A pesticide mixture was used for method development to study residues in various vegetable products sourced from China. For the high-S shale sample and S-compounds in fuel samples, chemical classes in 2D space were readily quantified. For the phosphate ester mix in 5% diesel and chemical weapon materials, matrix was completely transparent, but trace P-compounds at trace level were easily reported.

Multiresidue Screening of Pesticides in Dried Cocoa Beans using IMS-QTOF

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Multiresidue screening method for the analysis of pesticide residues in dried cocoa beans was validated and applied to imported and domestic cocoa beans samples. The screening method covers 20 pesticides (insecticides, fungicides, herbicides) of different chemical classes. The method was based on modified QuEChERS (Quick Easy Cheap Efficient Rugged Safe) extraction method and detection using ion mobility quadrupole time of flight mass spectrometry (IMS-QTOF). IMS allows for the measurement of the collision cross section (CCS), which provide information about the charge, shape and size of the pesticide compounds. Hence, additional identification tool in the form of CCS value provide more confidence in the identification process and at the same time lessening the probability of false positive during the pesticide screening process. Finally, a database of pesticide residues that consist of accurate mass, retention time, fragment ions, and CCS values was developed for cocoa beans matrix and applied to the pesticide residues monitoring programme.

Nano-IR spectroscopy and imaging of malaria infected red blood cells

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AFM nano-infrared (AFM-IR) spectroscopy is fast becoming a powerful technique to interrogate the nano structure of materials and to study the molecular phenotype of cells and tissues at the nano-scale. One limitation of the technology, to date, is that the maps generated are univariate in nature and only show either the absorbance plotted against a single wavenumber value or a ratio of two absorbance values. Here we apply multivariate imaging analysis, normally used in the treatment of hyperspectral images (HSI) from diffraction limited IR microscopy, to generate multicomponent AFM-IR maps (HSI-AFM-IR) that can be used for subcellular structural identification. This was achieved by converting the discrete spectral points into a hyperspectral line spectrum prior to multivariate image reconstruction. The approach was used to generate multi-compositional maps of subcellular structures in *Plasmodium falciparum* infected red blood cells including the food vacuole, lipid inclusions and the nucleolus by their chemical localisation according to the intensity of haemozoin, haemoglobin, lipid and DNA IR marker bands, respectively. The high spatial resolution HSI-AFM-IR can be used to detect subcellular components without the need for cell sectioning or addition of any immunological or biochemical staining agents. HSI-AFM-IR has the capacity to be used as a phenotypic probe of the malaria parasite to study its life cycle or to investigate the phenotypic response to antimalarial drug resistance.

NANOSCALE CLUSTERING OF INTEGRIN-BINDING LIGANDS REGULATES ENDOTHELIAL CELL ADHESION, MIGRATION, AND PROLIFERATION: NOVEL MATERIALS FOR SMALL DIMETER VASCULAR GRAFT APPLICATIONS

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Cardiovascular disease remains a leading cause of death worldwide. The development of blood compatible biomaterials could relieve this burden by enabling the development of improved cardiovascular devices such as small diameter vascular grafts. An attractive strategy for improving blood compatibility is to generate biomaterials that foster a confluent and functioning endothelial cell layer. Several strategies have been explored to improve endothelialization, but no blood compatible grafts with the ability to promote endothelialization have obtained commercial success as of yet. The lack of a blood compatible interface is one of the most pressing challenges in the biomaterials field.

In this work, we aim to test the hypothesis that biomaterials functionalized with nano-scale clusters of integrin-binding peptides will improve the endothelialization of the materials by promoting the clustering of integrin receptors and formation of focal adhesion complexes. To test this, we synthesized a low-fouling methacrylate-based polymer using RAFT polymerization that enabled the preparation of surfaces that displayed either randomly distributed or nano-clustered RGD ligands. We then assessed the endothelial cell adhesion, proliferation, and migration on the surface of these materials. The results of cell adhesion and proliferation are shown in Figure 1. Very low levels of cell adhesion and proliferation were observed on materials containing no RGD peptide or materials functionalized with the nonsense RGE peptide. The cells were able to adhere and grow on all RGD-containing surfaces. The adhesion and proliferation of cells improved by nano-clustering of RGD peptides compared to randomly dispersed peptides, at a constant peptide global density. Additionally, the migration results illustrated that the presence of nano-scale clustered ligands could increase the cell motility on these materials.

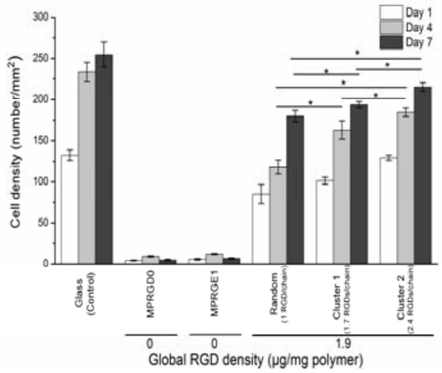

Figure 1. HUVECs adhesion and proliferation on polymers at days 1, 4, and 7. Random surfaces were composed of polymer chains with an average of one RGD per chain that were distributed randomly on the interface. Nano-clustered surfaces Cluster1 and Cluster2 were generated by blending the functionalized polymer chains (containing an average of 1.7 and 2.4 RGDs per polymer chain, respectively) with non-functionalized polymer chains. Global RGD density was kept constant at 1.9 µg peptides per mg polymer. 4.4×10^4 cells/cm^2 were cultured (n=3). *$p<0.05$.

Nano-sponge for active-targeting anti-cancer drug delivery

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Next to cardiovascular disease, cancer is the second leading cause of disease-related death. Chemotherapy is a commonly used therapeutic strategy for cancer treatment. However, severe side effects of anticancer drugs are recognized as a major problem.

The pharmacological properties of drugs can be improved by encapsulating drugs in nanoparticles (NPs), called as NP-based drug delivery system (DDS). Targeting cancer cells is, however, well known to be the key issue of any cancer therapy, including drug delivery system. Many solid tumor cells overexpress a transmembrane receptor, called CD44. The specific ligand for this receptor is Hyaluronic acid (HA), which can be applied on drug delivery systems in order to target different types of cancer cells. Intracellular barriers also limit the efficiency of the therapy. The eukaryotic endosomal system is known to hinder the achievement of the target. Polyethylenimine has been widely applied on DNA transfection procedures to avoid the endosomal system and increase the efficiency of DNA delivery into the nucleus.

In this contribution, we propose a simple and efficient method to develop a drug delivery system based on the polymeric functionalization of mesoporous silica nanoparticles filled with cancer drug (doxorubicin) and organic crystal consisted of mono-drug molecules. The nanoparticle surface is first functionalized with Polyethylenimine at appropriate pH. Afterwards, the amino groups on the surface are used to covalently bind HA resulting in a second polymeric layer. We tested the efficiency of our delivery device by inserting the functionalized nanoparticles into cancer live-cells.

Naphthalene Diimides as Versatile Components for Redox- and Photo-active Materials

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ABSTRACT TEXT

Naphthalene diimides are a versatile compound with suitability for a range of energy-related applications such as energy transduction, use in organic field-effect transistors and other optoelectronic devices. Their redox properties are similar to that of ubiquinone, and as such makes them suitable for studying the factors that govern electron and energy transfer processes such as those used in photosynthesis. This presentation will describe a range of systems we have prepared from their chemistry, supramolecular interactions and photophysical/electrical properties.

New Hybrid Materials Based On Carbon Dots For Self-enhanced Electrochemiluminescence

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A large variety of sensing and diagnostic techniques for the detection of chemicals and biological analytes are based on fluorescence, a very sensitive, easy, versatile and cheap detection. An interesting way to create the excited state of a molecule is by Electrochemiluminescence (ECL) since this technique does not require an excitation source and can be applied in highly absorbing media. In ECL the light emission is generated by a process in which species generated at electrodes, with the support of a reducing or oxidizing agent, a co-reactant, undergo high-energy electron-transfer reactions to form emissive excited states.[1] The most employed ECL luminophore is Ruthenium(II) tris(2,2'-bipyridyl) ($Ru(bpy)_3^{2+}$) because of its luminescence efficiency, reversible electrochemical behavior, chemical stability and versatility.[2] In the last years, beside the efforts to improve the luminescent label, some interests were also devoted to find new alternatives to the toxic co-reactant tripropylamine (TPrA). In this contribution, we present Amine-rich nitrogen-doped carbon nanodots (NCNDs) used as co-reactant in ECL processes. Primary and tertiary amino groups on NCNDs have been studied as co-reactant sites for $Ru(bpy)_3^{2+}$, showing their eligibility as powerful alternatives to TPrA. We also report the synthesis and ECL behavior of a new covalently-linked hybrid of NCNDs and $Ru(bpy)_3^{2+}$. Notably, the NCNDs in the hybrid act both as carrier for ECL labels and as co-reactant for ECL generation. As a result, the hybrid shows a higher ECL emission as compared to the combination of the individual components, suggesting the self-enhancing ECL of the ruthenium complex due to an intramolecular electron transfer process.[4]

Acknowledgement

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New Materials from the Oxime Click Reaction: Degradable Polymers to Hormone-Releasing Gels

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The oxime click reaction, previously utilised almost exclusively for bioconjugation, has recently gained significant attention for applications in material science and is fast becoming a valuable tool for the synthesis of novel materials. The attractive properties of the oxime bond; very rapid formation, high selectivity/bioorthogonality, dynamic covalent properties and high yielding reactions has led to its use in the development of self-healing hydrogels, stimuli-responsive dynamic materials, bio-adhesives and bio-compatible hydrogels. Our research is focused on synthesising new materials via oxime click chemistry and investigating their dynamic properties for a variety of applications. This presentation will highlight three new oxime-based materials developed in our lab; dynamic step-growth polymers and self-healing hydrogels, stimuli-responsive hydrogels for the capture, culture and release of various cell types and a novel class of steroid hormone releasing polymer.

New Measurement Techniques Improve Understanding of Biogeochemical and Contaminant Processes

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ABSTRACT TEXT

Natural environments can be highly variable over time or heterogeneous over distance. Some are both. This makes it challenging for monitoring and research studies to obtain data that is representative and accurate, which are both required to understand environmental processes and manage contaminants. My research has focussed on use of passive sampler devices (PSD) and other techniques to address these challenges. PSDs of interest are the related DET (diffusive equilibrium in thin films) and DGT (diffusive gradients in thin films) techniques.

DET and DGT methods have been developed to allow measurement of two-dimensional, mm-resolution and highly representative measurements of distributions of key sediment porewater solutes (Fe(II), sulfide, phosphate, alkalinity). The Fe(II) and sulfide measurements generally represent the sub-oxic and the anoxic biogeochemical zones, respectively. Use of these techniques has confirmed that many coastal sediments exhibit a high degree of heterogeneity, which has particular implications for the use of conventional sampling methods that often cause unstable porewater solutes to react and form precipitates.

DGT methods have also been developed to measure nitrate, ammonium and phosphate in surface waters. Concentrations of dissolved inorganic nutrients change considerably during high flow events and can even vary over diurnal cycles in productive waters, especially for nitrogen species. The DGT techniques were demonstrated to provide time-weighted average (TWA) concentrations that were highly representative of the changing nutrient concentrations and thereby should be considered for use with investigative monitoring. A TWA sampler for particulate substances is also being developed for which I will present preliminary results.

New Michael Acceptor and Rhenium(I) [^{18}F]radiolabelling Methods for Radiopharmaceutical Development

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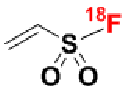
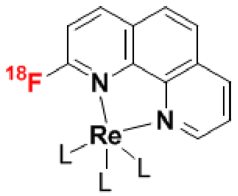
Positron emission tomography (PET) is a powerful molecular imaging technique with well-established diagnostic applications.[1] One of the initial steps in any PET radiotracer development program is radiolabelling of biological vectors. For this purpose fluorine-18 remains one of the most popular radioisotopes owing to its clean decay profile, almost ideal half-life and low positron energy. Not discounting these considerable benefits, SPECT based radiotracers, however, remain the world's most widely utilised diagnostic radiopharmaceuticals. This is in large part due to their simple preparation and straight-forward patient administration. And therein lies the challenge, which is to develop similar, straightforward methods for fluorine-18 which will ensure it remains an important class of PET radionuclide into the future.

ANSTO Human Health researchers and the Radioisotopes and Radiotracers platform are exploring new methods for radiolabelling with fluorine-18, with particular emphasis on operationally simple (non-HPLC, cartridge based), fast, high yielding, and water compatible methods. Our ultimate goal is to radiolabel vectors in formulation media (saline or other) that can be directly injected into animals and/or patients for pre-clinical and clinical studies. Currently we are exploring the microfluidic radio-synthesis, purification and bio-conjugation properties of two new radiolabelling methods / synthons. The first is the new [^{18}F]synthon - ethenesulfonyl fluoride ([^{18}F]ESF) - shows significant promise as a mild, selective and water compatible reagent for [^{18}F]radiolabelling. The second is a direct Rhenium(I) promoted S_NAr fluorination method that is a unique, aqueous based, high yielding route to potential dual modal PET / near-IR optical imaging tools.



[^{18}F]ESF



Rhenium (I) promoted fluorinations

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New polymer from lignin degradation fragments

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Lignin is the second most abundant renewable biopolymer after cellulose, and both represent more than 70 % of the worldwide biomass. Its structure is a complex 3D network of phenol compounds liked by C-C (carbon-carbon) or C-O-C (carbon-oxygen-carbon) bonds, thus representing a promising source of aromatic compounds. However, its high recalcitrance to degradation have strongly hindered any valorisation of lignin to high added value chemical. Up to date very few chemicals have been successfully isolated from lignin such as vanillin or syringaldehyde. They represent, for now, the most promising biobased building-block for synthesis of monomers, opening pathway to aromatic renewable polymers. The reported work will mainly focus on thermoplastic, as thermoset from lignin have been widely reported in literature. Vanillin and syringic acid have been used as building-block for monomer synthesis yielding a series of different polymers, focussing on new polymerisation pathways that have never been reported for lignin repolymerisation.

New Reaction Discoveries in Vinyl Azide Chemistry and Cobalt Catalysis

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Discovery of new reactivity has led to many fundamental reactions now used routinely in academic and industrial organic synthesis.[4] In this presentation two unexpectedly observed reaction outcomes will be discussed, along with preliminary mechanistic investigations and potential synthetic applications;

In studies directed towards ester alkylation with azide-containing eletrophiles, a direct synthesis of industrially important *N*-vinyl amides was unexpectedly observed. This reaction is likely to proceed via an unusual [3+2] azide-enolate cycloaddition. The process appears to involve rarely reported vinyl azide, generated *in situ*, that lowers the cycloaddition activation energy, a finding supported by quantum computational analysis. These results may pave the way to new atom-efficient methods for amide synthesis but more intriguingly suggest that (cautious) re-evaluation of vinyl azide as a practical synthetic reagent may be warranted.

Cobalt is widely used in catalytic applications, including the well-established Jacobsen hydrolytic resolution of racemic epoxides. In using resolved epoxides for ring expansion to oxetanes using a sulfoxonium ylide, traces of the cobalt HKR catalyst showed a remarkable ability to catalytically divert the course of the reaction to selectively give unexpected homoallylic alcohol products. An expanded survey of transition metal catalysts has confirmed that cobalt salts are unique in possessing this activity. The reaction is an unusual example of cobalt(salen) catalysed epoxide ring-opening by a carbon nucleophile. Our preliminary mechanistic proposals and utility in synthesis will be discussed.

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New Reactions for Natural Product Synthesis and Drug Discovery

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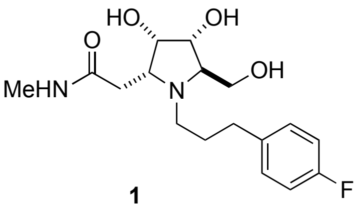
Our research program focuses on the identification of concise and stereoselective synthetic methods that can be readily applied to medicinal chemistry campaigns or the total synthesis of natural products. A longstanding theme in our group is the use of chlorohydrins as building blocks for the synthesis of stereochemically rich heterocycles.[1] These efforts have recently led to the discovery of iminosugars that are brain permeable and potent of inhibitors of the enzyme OGA, and thus represent potential leads for the treatment of Alzheimer's Disease (e.g., **1**).[2,3] This lecture will summarize our efforts in the development of new strategies for the synthesis of stereochemically rich heterocyles and their application in medicinal chemistry campaigns. In addition, our recent advances in the photocatalytic fluorination of C-H bonds (e.g., **2** → **3**),[4] and the application of this late-stage functionalization strategy to medicinal chemistry,[5] process research[6] and the synthesis of positron emission tomography (PET) radiotracers[7] will be discussed.



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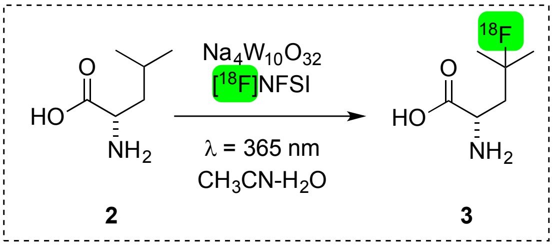

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New Reactivity Using Amphoteric Isocyanates

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ABSTRACT TEXT

Most agrochemicals and pharmaceuticals contain nitrogen atoms in their structure, and C-N bond forming reactions account for approximately 15% of the reactions used in pharmaceutical R & D efforts. Our group has long been interested in reactions and strategies to rapidly assemble nitrogen-containing molecules, initially using cycloadditions reactions of hydroxylamine and hydrazine derivatives. These efforts have led to unexpected opportunities involving heteroatom-substituted isocyanates. While normal carbon-substituted isocyanates are ubiquitous ($10B/year market, >100,000 publications and patents), only a few dozen publications feature *O*- and *N*-isocyanates. In contrast to normal isocyanates, *O*- and *N*-isocyanates are amphoteric: they possess nucleophilic and electrophilic sites that account for some of the side reactions such as dimerization that have hampered their use. Recently, our group has shown that controlled reactivity is possible through the use of masked isocyanate precursors, that allow in situ formation of *O*- and *N*-isocyanates . Recent results will be presented, highlighting their synthetic potential for the incorporation of the N-NCO and O-NCO motifs in bioactive molecules, in heterocycles, and their use in new C-N bond forming reaction

New sampling techniques for selective analysis of food volatile markers

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ABSTRACT TEXT

Trace food volatiles usually contain potential but important markers for food safety analysis and quality control. Nowadays, it still remains a great challenge to develop efficient sampling techniques for trace food volatiles due to their strong volatility of trace food volatiles from real samples with complex matrice. Development of selective sampling techniques with large extraction capacity benefits the sampling efficiency of trace food volatile markers coupled with suitable detection techniques. In our previous reports, a series of novel nanoscale enrichment media and methods were developed which mainly focused on the improvement of sampling capacity and selectivity for trace food volatile markers from real food samples. The proposed sampling methods such as sorbent tube, headspace solid-phase microextraction (SPME) and so on were actually applied for evaluating and monitoring freshness of seafood during storage based on the various chromatographic characteristics of volatile markers at different storage phrases. Also, the combination of multiple data-processing methods such as normalization, principle component analysis and common model can provide more detailed representative bio-information from chromatographic characteristics of seafood volatiles during storage. It is expected that these new sampling techniques for trace food volatile markers could benefit the food safety analysis and quality control coupled with efficient data-processing methods.

New Synthetic Applications of Electron-Rich Alkenes with Ylide Character

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N-Heterocyclic Olefins (NHOs), the alkylidene derivatives of the prevalent *N*-heterocyclic carbenes (NHCs), have very recently emerged as efficient promoters for some interesting chemical reactions.[1-5] Due to the donating effect of the heteroatoms and the ability to accommodate a positive charge on the partially aromatized *N*-heterocyclic system, the exocyclic C-C double bond is highly polarized, making the α-carbon very electron-rich and therefore rendering it a reactive nucleophilic center. Thus, NHOs can act as strong Brønsted/Lewis base organocatalysts for various types of organic transformations.[6] Our recent studies on the novel applications of NHOs as versatile organocatalysts[7-9] and stoichiometric reagents[10] for several important chemical transformations will be discussed.

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New synthetic methods for exploring π-rich molecular space.

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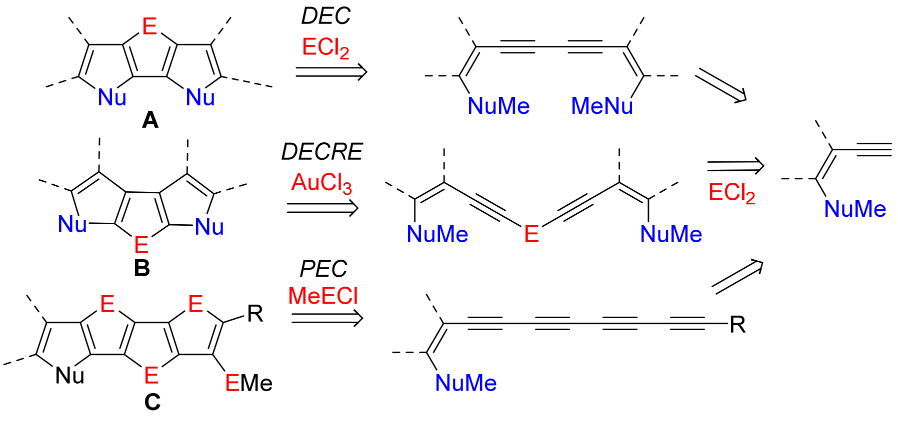
The field of organic electronic and photonic materials has witnessed explosive growth in the last 10-15 years and become a major area of study within organic chemistry.[1] The extended π-networks formed from fusing aromatic and heteroaromatic rings to give acenes and heteroacenes is central to the generation of photonic activity, where interactions between photons and π-electrons are exploited in a wealth of new and emerging technologies.[1] Some of these technologies have already attained commercial success, such as organic light emitting diodes (OLEDs) and other applications are continuously emerging and including bioimaging, organic solar cells and light-driven molecular motors. The heteroacene arrangements depicted in Scheme 1 represents a form of conjugated (**A**/**C**) and cross-conjugated (**B**) polyene that are considered a privileged structural classes in photonics. This paper describes three new methods that convert readily accessible alkyne substrates into valuable heteroacenes: double-electrophilic-cyclisation (DEC), transition metal-mediated DEC-reductive-elimination (DECRE) and polyelectrophilic cyclisation (PEC) (Scheme 1). These are aiding our exploration of π-rich molecular space and its photonic applications.

Scheme 1: Innovative chemical methods, DEC, DECRE, PEC afford π-rich acenes



E = S, Se, Te. Nu = O, S, Se, NMe
DEC = double-electrophilic-cyclisation
DECRE = double-electrophilic-cyclisation-reductive-elimination
PEC = polyelectrophilic cyclisation

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New visible light-responsive lyotropic liquid crystalline delivery material

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Light-responsive lyotropic liquid crystalline mesophases are of increasing interest in the field of drug delivery because they provide a potential means of controlling the release of drugs with extreme accuracy and in a non-invasive manner. Such "on-demand" delivery systems might provide improved treatment options for diseases such as age-related macular degeneration. To date, most developed light-responsive systems require UV irradiation to achieve activation, which is less than desirable because of the very low tissue penetration capabilities and damaging effects of UV light on healthy tissue. This study aims to develop liquid crystal-based drug delivery systems incorporating green light-responsive photo-switchable molecules. One such molecule is **D1**, an alkylated donor acceptor Stenhouse adduct that undergoes a transition from an extended hydrophobic triene form to a compact zwitterionic cyclopentenone form upon visible light irradiation (Figure 1A).[1,2] Small angle X-ray scattering (SAXS) experiments have shown that the photo-isomerization of **D1** upon visible light irradiation (532 nm) is able to disrupt lipid packing within a host liquid crystalline system prepared from 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC) and lauric acid, inducing a phase transition from lamellar phase (slow-release pattern) to a mixture of reversed cubic phase (rapid-release pattern) and reversed hexagonal phase (Figure 1B). This is a successful proof-of-concept that irradiation of **D1**-doped liquid crystals with visible light can induce a reversible change in nanostructure, thereby providing a method for achieving controlled release of drugs from liquid crystalline delivery systems.

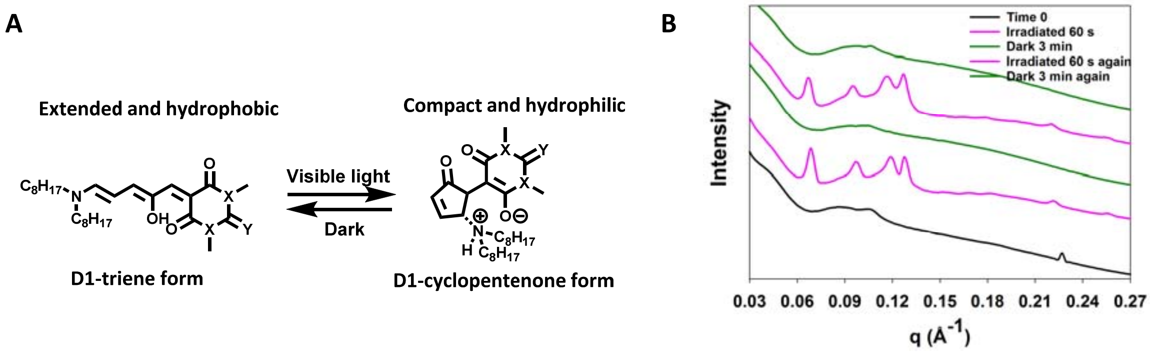

Figure 1 *(A) The photo-isomerization of **D1**. (B) The SAXS profiles of DLPC/lauric acid liquid crystals with **D1** (4%, w/w) upon two cycles of irradiation, indicating a phase transition from lamellar phase to a mixture of reversed cubic phase and reversed hexagonal phase upon irradiation.*

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NISEP – ENHANCING EDUCATIONAL OUTCOMES FOR INDIGENOUS YOUTH

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“Can you help us help our youth?” This request from Aboriginal Elders of northern New South Wales, Australia, led to the formation of the National Indigenous Science Education Program (NISEP). NISEP uses science to place Indigenous youth in leadership positions so they gain the confidence, motivation and skills to engage with their schooling and consider pathways to higher education. The program targets secondary students from low socioeconomic and rural/regional areas. It is a unique collective of Aboriginal Elders, science academics and high school staff, committed to helping the educational attainment of Indigenous youth in a meaningful way. Our model of engagement involves secondary student leaders demonstrating predominantly chemistry activities to junior students, their peers, family and the general public at our in-school, community and university based events. We currently incorporate 15 high schools and 3 universities. Key aspects of NISEP’s success include our commitment to the long-term mentoring of our students, the provision of university academics and students as role models, and our best ethical approach of working inclusively with schools and Indigenous communities. After participating in a NISEP event, 82% (n=690) of students have expressed an increased interest in science and 72% (n=537) an increased desire to complete school and go onto tertiary education. They have also consistently reported that NISEP has provided them with increased confidence and educational aspirations. This presentation will describe our achievements and highlight key research outcomes arising from intensive interviews and focus groups we have undertaken with our NISEP student leaders and school staff.

Nitroxide releasing polymers to protect against bacterial biofilms

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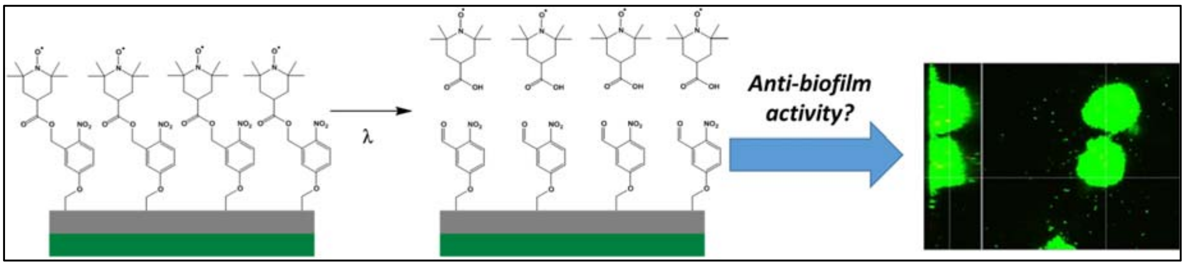
Biofilms are highly organised colonies of bacteria and other microorganisms on a surface. These colonies show a high level of structural complexity, which helps to protect the microorganisms from removal from the surface by both physical and chemical processes. Biofilms can cause major issues for industry, for example through the fouling of ship hulls or food processing plants. They are also implicated in the majority of nosocomial infections where they can show increased resistance against conventional antibiotic therapy.

Our research group has shown that small molecule nitroxides (persistent and stable free radical species) are able to inhibit the formation of biofilms on a surface, as well as being able to disperse existing biofilms. In this project, we look to extend these molecules further by designing polymeric materials bearing pendant nitroxide groups, which are bound to the polymer chain via stimuli-responsive linkers.

This presentation will detail our efforts to synthesise and characterise thin films containing pendant nitroxide units, bound through a light sensitive *o*-nitrobenzyl linker. The physical characterisation and stimuli-responsive degradation of the polymers will be presented and compared to small molecule systems.



NITROXIDE-CONTAINING AGENTS FOR BIOFILM REMEDIATION

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The adhesion of bacteria to surfaces and their subsequent ability to aggregate into colonies called biofilms is a significant global problem in numerous applications, particularly as biofilms display an inherent resistance to antimicrobial agents. Low concentrations of the diatomic free radical nitric oxide has been shown to disperse bacterial biofilms to free swimming planktonic bacteria,[1] which has led to the development of coatings that release nitric oxide. However, the non-systemic delivery of gaseous nitric oxide remains challenging as nitric oxide is an extremely reactive molecule with a very short half-life. As an improved strategy, we have recently reported the ability of nitroxides (persistent and stable free radial species that are sterically hindered versions of nitric oxide) to inhibit bacterial biofilm formation and/or disperse existing biofilms (Figure 1).[2] This presentation will discuss these results and detail our current work towards the design and development of novel nitroxide-containing anti-biofilm agents and materials.

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NON-TARGETED SCREENING OF NEW PSYCHOACTIVE SUBSTANCES USING LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY

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The proliferation of new psychoactive substances (NPS) in recent years has resulted in the development of analytical methods for the detection and identification of known and unknown NPS analogues. Simultaneously, liquid chromatography-high resolution mass spectrometry (LC-HRMS) has gained popularity in forensic toxicology and sports anti-doping laboratories by providing a highly versatile analytical platform for targeted, suspect and non-targeted screening of NPS in biological samples. The ability to acquire accurate mass data in full scan and MS/MS modes using data independent acquisition (DIA) techniques enables retrospective interrogation of results using 'mining' strategies to provide intelligence concerning NPS misuse. Presently, there is no single data processing technique that can be adopted for the reliable detection of novel analogues in non-targeted analyses, however, the combination of reported techniques can be effective for their putative identification. This may include differential analysis, mass defect filtering, product ion searching and neutral loss filtering.

This presentation will illustrate the application of LC-HRMS for the analysis of phenethylamines and synthetic cathinones in human urine, including the development of non-targeted screening strategies to detect novel analogues without the need for certified reference materials (CRMs) or comprehensive mass spectral libraries. It is envisaged that this methodology will be translated to other classes of substances in complex matrices such as equine plasma and urine.

Evidence of the NOO peroxy radical discovered in the photoelectron spectrum of NO_2^-

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ABSTRACT TEXT

NO_2 is a key component of photochemical smog, and an important molecule in the Earth's atmosphere. Through the implementation of velocity-map imaging, both the energetic and angular information of the photoelectrons are acquired with 100% collection efficiency, allowing for multiple detachment/dissociation channels to be observed simultaneously. This benefit is highlighted in our measurements of NO_2^-, where unexpected additional high eKE photoelectrons are revealed. The surprising high eKE structure persists at detachment energies lower then the EA of ONO- (2.273eV) [1], confirming that this previously unseen electron structure can not arise from the standard C_{2v} isomer of NO_2^-. Through further investigation, this work shows that the additional high eKE structure observed is the result of another isomer of NO_2^-, NOO. While the possibility of a peroxy NO_2 isomer has been postulated in the literature, there has been no previous conclusive evidence that a stable NOO isomer exists [2, 3, 4]. By providing the first direct measurement of the NOO isomer, this work may have a significant impact on our understanding of this vital NO_2 molecule, a result with many possible implications in atmospheric science.

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NOVEL 2D GRAPHENE-LIKE MEMBRANES FOR ENERGY APPLICATIONS

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Carbon structures have been extensively studied over recent decades as energy storage materials. One of the industry applications is as the anode of lithium (Li) ion batteries. Graphite, a layered material consisting of sp^2 bonded carbon sheets is currently the predominant anode material offering a theoretical capacity of LiC_6 with Li inserted between the layers. To achieve higher storage capacity, novel anode materials such as carbon allotropes, carbon nitrides or graphene composites, are widely being pursued. Some materials that surpass the capacity of graphite for Li storage have been identified.

We investigate the Li storage capacity of novel porous graphene-like 2D membranes. These include porous graphitic carbon nitrides, g-C_3N_4, g-CN, hC_2N, and 2D polymer membranes g-$C_xN_yH_z$, carbon only membranes such as graphenylene and biphenylene, and siligraphenes, g-C_3Si and g-C_7Si.

Density functional theory (DFT) calculations are employed to obtain the maximum Li storage capacity. We also calculate diffusion barriers for the Li movement from one site to another to determine the mobility of the Li atoms. In addition to this we also show how the Li binds to the membrane by consideration of the charge density distribution and the charge transfer from the Li to the membrane. The volume change of the material on the insertion of lithium is determined by employing a bilayer or bulk configuration of the material.

NOVEL ANTIOXIDANT ACTIVE COMPOUND FROM AN ENDOLICHENIC FUNGUS, *Penicillium citrinum*

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Fungi live asymbiotically in lichen thalli are known as endolichenic fungi and they are considered as new source of bioactive secondary metabolites. Endolichenic fungi are known to produce novel structurally diverse bioactive compounds. In the present study, isolation of novel bioactive compound is discussed from an endolichenic fungus, *Penicillium citrinum*. *Penicillium citrinium* was isolated from the lichen *Parmotrema* sp. and grown in large scale. Ethyl acetate extract of the fungus was subjected to bioassay guided fractionation using column chromatography and preparative thin layer chromatography to isolate bioactive compounds. *In vitro* antioxidant activities of the pure compounds were investigated using the DPPH scavenging methods with micro plate assay. A new bioactive compound, 10-Ethylidene-2,4,9-trimethoxy-10,10a-dihydro-7,11-dioxa-benzo[b]heptalene-6,12-dione, named as PP-PC-03 **(1)** together with PP-PC-01 **(2)** and PP-PC-02 **(3)** were isolated from *Penicillium citrinum*, a fungus occurring in the lichen, *Parmotrema sp.*, collected from Hakgala Botanical Garden in Sri Lanka. The structure of PP-PC-03 **(1)** was established on the basis of their spectroscopic data. The antioxidant assay results revealed that PP-PC-02 **(2)** and PP-PC-03 **(1)** showed moderate antioxidant activities with IC_{50} values 159.6±22.3 μg/mL and 120.1±11.7 μg/mL respectively and PP-PC-01**(2)** showed strong radical scavenging activity in the DPPH assay with IC_{50} value of 68.6±4.3 μg/mL. The results suggest that new compound, PP-PC-03 **(1)** can be developed as a potent antioxidant to prevent radical formation as that help to prevent noncommunicable diseases in human body.

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Novel dendritic polymers as enhanced non-viral gene delivery vehicles

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ABSTRACT

Non-viral gene delivery systems promise to be the long-term future for delivering gene therapies in a safe and controllable manner. However, non-viral vectors commonly have to balance gene delivery efficiency with the inherent toxicity of these highly charged delivery agents. Further to this, the ability for consistent co-transfection and achieving this in a broad range of cell lines has also been relatively elusive for these types of delivery agents. Here we describe the design and synthesis of a dendritic polymer using ATRP, and evaluate its performance as an efficient transfection agent. First, we demonstrate how the novel dendritic polymer results in self-assembly with DNA to form positively charged nanoparticles. Second, we will report the transfection efficiency and biocompatibility of these nanoparticles and compare it the gold standard, Lipofectamine 2000. Finally we will demonstrate how the novel design of the polymers to enable dendron flexibility affected the success of both single and co-transfections in a relatively difficult-to-transfect human breast cancer cell line (MCF7), while maintaining cell viability. We feel this polymer formulation developed represents a new class of highly efficient agents for gene delivery with applications both *in vitro* and *in vivo.*

Novel fixed-charge photo-labile derivatives for structural elucidation of isomeric lipids.

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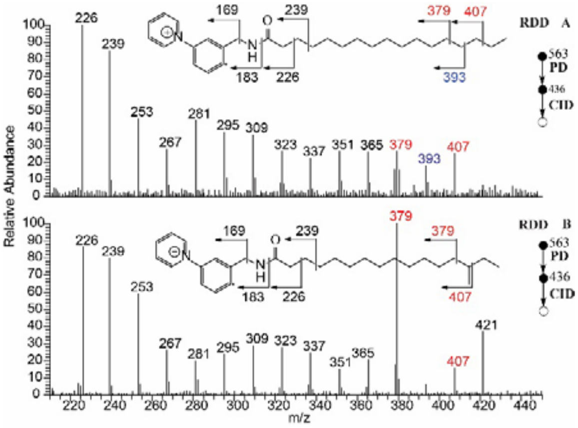
Abstract

Derivatization of fatty acids (FAs) is widely used in conjunction with gas-chromatography mass spectrometry to facilitate identification and quantification of the fatty acids extracted from biological samples (Bollinger, 2010).[1] However, limitations in this approach for differentiation of isomeric FAs have been widely reported. Fixed-charge derivatization strategies developed for improving analytical sensitivity by electrospray ionisation mass spectrometry (ESI-MS) have also proven to be informative for differentiating isomeric FAs. This approach relies on the generation of diagnostic charge-remote product ions upon collision-induced dissociation (CID) of the FA derivative. However, the abundance of these product ions is low relative to competing charge-directed processes which can cause ambiguity in the analysis of complex mixtures. An alternative strategy employed by our group involves preparation of FA derivatives incorporating a photo-labile C-I bond (Pham, 2013).[2] Photo-dissociation (PD) of the mass-selected derivative with a single laser pulse of 266 nm photons produces abundant radical ions, which initiate C-C bond dissociation along the FA backbone with high sequence coverage. In this project, we have designed and synthesized a novel derivatization reagent *N*-(3-aminomethylphenyl-4-iodophenyl)pyridinium (I-AMPP) that combines the above strategies to improve sensitivity and specificity. I-AMPP derivatization and PD analysis protocol has been deployed on isomeric FAs including isomers differing in the sites of unsaturation and positions of methyl chain-branching and hydroxylation. In all cases distinctive product ions were observed allowing unambiguous differentiation of isomeric species. In this presentation, synthesis and application of I-AMPP for discrimination of isomeric fatty acids in LNCaP prostate cancer cell lines will be presented.



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Novel nanosensors for the combined isolation and detection of proteins

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ABSTRACT

An ultrasensitive and reproducible nanosensing methodology for the combined isolation and SERS detection of protein has been developed and demonstrated for the determination of the environmental toxin, Microcystin-LR (MC-LR), in water and blood plasma. For the isolation of the toxin from complex matrices, functionalized extractor nanoparticles that comprise gold coated magnetic and anti MC-LR antibody Fab' fragments have been developed. The antibody fragments were attached to the extractor nanoparticles using oriented immobilization strategy to maximize the capturing efficiency of the toxin. After the selective capture and release of the purified MC-LR from the extractor nanoparticles, the protein was rapidly screened on paper-based SERS and gold coated silicon nanopillar substrates using handheld Raman spectrometer. The SERS enhancement factor of the paper-based substrate was 2.5×10^6. The nanopillar substrate was used for the quantitative analysis of the toxin in blood plasma to a low quantification limit (LOQ) of 10fM (R^2=0.9975). The SERS determination of MC-LR was cross-validated against ELISA. By using target-specific antibody fragments, the new methodology can be extended to the rapid extraction and detection of other toxins and proteins in environmental, forensic, and pathology samples.

Novel PET tracers for imaging resistance and response in cancer

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In the era of molecularly targeted therapies, spectacular outcomes have been rather limited to short durations due to lesion heterogeneity or clonal evolution resulting from treatment selection, mutations or upregulation of alternative pathways. The tumor heterogeneity problem results in poor patient outcomes or failure of clinical trials with efficacious drugs, due to our limited ability in selecting responders from non-responders. PET has ability to investigate disease biology for each lesion and provide a meaningful rationale for differentiating responders from non-responders and thereby serve as a prognostic indicator. The talk will focus on how insights from the biology of the disease can be utilized in the design and development of PET probes to develop functional imaging biomarkers that aid us in predicting whether the tumor will respond or resist, to a drug or class of drugs. This will be illustrated using prostate and breast cancer examples. Prostate cancer is a slow growing cancer that is driven by androgen receptor (AR) signaling pathway but resistance eventually develops. The talk will discuss how a novel PET imaging that targets AR repressed gene integrin beta4 can be used to follow the progression of disease and help determine best course of therapy. For breast cancer, the talk will focus on how PET imaging with a novel Hsp90 inhibitor is being developed as a companion diagnostic for determining intratumoral drug concentration and kinetics. The ultimate goal is to aid the development of personalized and precision cancer treatments that can improve patient outcomes.

N-oxide chemistry as a universal fluologenic molecular switch for labile Fe(II)

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Iron plays a number of biologically and pathologically important roles in our body. Labile iron, In particular, Fe(II) iron is a key element of oxidative stress as well as iron transport in living systems.. However, studies of redox status of iron have remained challenging because of a lack of redox-state selective detection methods of iron species, in particular, labile Fe(II) ion. We previously reported rhodamine-based fluorescent probes which detect Fe(II) ion redox-selectively with turn-on readout by utilizing *N*-oxide chemistry[1,2] and have successfully applied the probes to reveal the functions of labile Fe(II) ion in various disease-models.[3–5] The N-oxide group works as Fe(II)-reactive site as well as fluorescence switch on the rhodamine scaffold. Recently, we have established a color series of Fe(II)-selective fluorescent probes on the basis of the *N*-oxide strategy, suggesting that our *N*-oxide chemistry could be a universal fluorogenic switch for Fe(II). I'll disclose the properties and possibility of our *N*-oxide strategy in the presentation.

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Nucleotide Functionalised Synthetic Polymers

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This paper outlines the synthetic methods for producing nucleotide functionalised synthetic polymers using reversible addition-fragmentation chain-transfer (RAFT) polymerisation. First a modified phosphoramidite approach is used to produce a monomer for the RAFT polymerisation. Four different monomers were prepared using protected nucleotides of adenine, thymine, guanine and cytosine. This was achieved by coupling 2-hydroxypropyl methacrylate (HPMA) to a 3'-deoxynucleotide, 5'-dimethoxytrityl-2'-deoxy nucleobase, 3'-[(2-cyanoethyl)-(*N*,*N*-diisopropyl)]-phosphoramidite (DCP), resulting in a HPMA-3'-deoxynucleotide monophosphate bioconjugate. Coupling of the HPMA to the DCPs was determined using ^{1}H nuclear magnetic resonance (NMR) spectroscopy and electrospray ionisation-mass spectrometry (ESI-MS) to confirm the substitution of the diisopropylamine with the HPMA. The coupling yield was determined to be >80% for each of the 4 nucleotides.

Each individual HPMA-3'-deoxynucleotide monophosphate bioconjugate was then polymerised using an azobisisobutyronitrile initiator and 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid *N*-succinimidyl ester as a RAFT chain transfer agent (CTA) at 70 °C. The kinetics of the polymerisation were measured with ^{1}H NMR spectroscopy using the change in peak area ratio of the vinyl peak at 5.4 ppm relative to the initiator and RAFT CTA agent peaks at 1.4-1.5 ppm indicating a 55% conversion in 5 hours. Following this time size exclusion chromatography was used to determine the polydispersity index of 1.3 and Mw of 13.5 kDa.

Deprotection of the bioconjugate was conducted with 2 successive workups. Firstly, heating with excess ammonia at 50 °C for 48 hours for deprotection of the nucleobase and phosphate. This was followed by isolation and treatment with concentrated acetic acid to remove the 5' hydroxyl protecting group. ^{31}P NMR spectroscopy was used following workup to confirm oxidation of the phosphorous from the P3 to P5 state. Current work is focussed on the conversion of the bioconjugate from a monophosphate to a triphosphate for use in enzymatic systems, specifically the polymerase chain reaction, for template polymer synthesis.

One-Electron Oxidation of DNA-Guanine Followed by Deprotonation: Structure-Dependent Reaction Pathways

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With the lowest oxidation potential among all the nucleobases, guanine (G) is extremely redox active and plays central roles in the processes of DNA oxidative damage and DNA charge transfer. Upon the interaction of photoexcitation or under the attack of potent radical oxidants, G is subject to a facile loss of an electron and forms a cation radical $G^{+\bullet}$ (hole) in DNA strand, initiating the hole transfer that makes DNA a charge transfer wire, or leading to a cascade of DNA oxidative damage events. $G^{+\bullet}$ may deprotonate or undergo nucleophilic addition reactions of water addition, leading to a variety of guanine lesion products (e.g., 8-oxoG, FAPY-G, imidazolone, and oxazolone) associated with the occurrence of degenerative diseases, cancer, and aging. To know the mechanisms and dynamics of guanine oxidation is critically important to understand DNA oxidative damage in the biological cellular process as well as to the development of DNA-based electrochemical devices. In this context, we have employed transient UV-vis absorption spectroscopy to directly monitor the one-electron oxidation of guanine followed by deprotonation within the duplex, triplex, and G-quadruplex DNA. We find that the reaction pathway is highly dependent on DNA structures in terms of hydrogen bonding, base stacking and solvent accessibility. Different from duplex DNA, unusual deprotonation behavior has been observed in G-quadruplex or triplex DNA. The remarkable structural effects on the reaction properties and dynamics of $G^{+\bullet}$ in DNA are unraveled, shedding light on DNA radical chemistry.

One-photon and Multiphoton Bacterial Imaging with Red-Emitting Dicyclometalated Platinum(II) Aggregates

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Long-lived excited state metal complexes are revolutionising many areas of photochemistry and photophysics. Amongst other transition metals, Pt(II) complexes, with their d^8 electronic configuration and 4-coordinate square-planar geometry, offer photophysical properties and reactivity which make them very different from the most studied d^6 metal complexes.

Our work focuses on the synthesis and characterisation of a new family of platinum(II) dyciclometalated complexes of the general structure [Pt(CNC)L], where CNC is a triphenylpyridine ligand and L a monodentate neutral species.

The photophysical and aggregation properties of the complexes have been investigated and studies on bacterial cells have been conducted, in order to assess the potential application of this family of compounds for bacterial imaging, that recently has been proposed as a promising technique to provide a deeper understanding of pathogens biology, as well as of the exact dynamics that are involved in bacterial infections and in antibiotic resistance development.

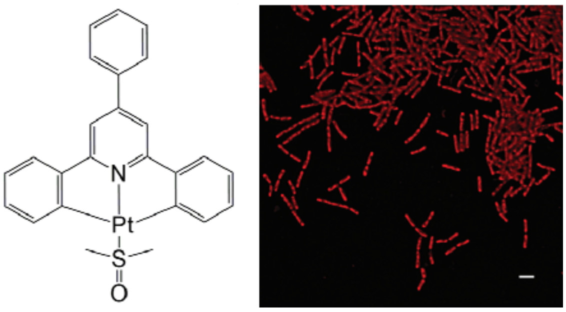

Figure 1. Example of complex and confocal microscopy image of B.subtilis incubated with the complex. (Scalebar 2 μm).

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Online strategies to better prepare and engage first year chemistry students in the laboratory

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ABSTRACT

The chemical laboratory has the potential to be a rich learning environment for students. The activities that students do before they enter the laboratory are critical to better maximise student engagement and enhance the learning experience. The aim of any pre-laboratory activity is to prepare the mind for learning in the laboratory. The traditional approach to pre-laboratory exercises usually involves reading the laboratory manual and answering questions. In recent times there has been increased activity to present the material from the laboratory manual as an online video and/or online quiz. In this talk we present the development and evaluation of two online interactive pre-laboratory activities, with the aim of enhancing preparation and engagement. The first activity is an interactive online pre-laboratory video. The video details the experimental procedure but at two points in the video the student is presented with a choice. Students can pick any of the choices presented to them in order to continue with the video. Students are given feedback on whether their choice had the desired outcome or not. The second activity was the development of a 360° image of the laboratory where students can navigate particular parts to increase familiarity with the surroundings. We evaluate the impact of the two activities through the use of online surveys and focus group interviews with students. We also compare the impact of these activities on students with a chemistry background from high school and those with no prior chemistry knowledge.

Open-Note Chemistry Exams as Opportunities for Meaningful Learning and Assessment

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Higher order cognitive skills (HOCS) are a critical graduate attribute particularly in STEM fields. HOCS can impact critical thinking skills such as problem solving and clinical decision making. Many educators attempt to evaluate and integrate higher order cognitive domains, necessary for critical thinking, by implementing open-book and/or open-note assessments. While open-note assessments have been used in chemistry education [1], the related literature is rather controversial with respect to their effects on learning, limited mostly to the teaching of psychology, and guidelines are lacking in terms of optimal implementation. In order address the issues related to open-note assessments we have studied the perspectives of multiple stakeholders, both students and educators.

We have investigated perceptions and study habits of students' participating in physical chemistry coursework and assessed via open-note exams, where students are allowed to bring and use their Individual Reference Cards (IRCs), constructed during the semester.

We have also sought the views of educators who have implemented open-note assessments in a range of subjects across Monash University. While the methods of implementation of open-note assessments vary between units, some common trends have emerged relating to positive influence of self-constructed IRCs on student engagement and learning.

Our qualitative and quantitative findings suggest that construction of IRCs promotes meaningful learning and that students' study techniques are positively influenced when expert guidance is provided.

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Optimisation of a novel compound class into potent antimalarial agents with oral *in vivo* activity

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ABSTRACT

The World Health Organisation (WHO) estimates that around 3.5 billion people, about half of the world's population, live at risk of malaria. Despite the roll out of preventive measures such as insecticide laced bed nets and new combination therapeutics, malaria still causes >480,000 deaths annually. Due to the threat of emerging drug resistance, the current arsenal of clinically used artemisinin combination therapies and drug candidates undergoing clinical assessment may not be sufficient in eliminating the disease. Thus, novel antimalarial therapeutics that target multiple stages of the parasite lifecycle are required to continually populate the antimalarial clinical portfolio.

Presented is an overview of antimalarial drug discovery programs at WEHI with a focus on the optimisation the 2-anilino quinazoline class (Gilson *et al J. Med. Chem.* 2017, 60, 1171−1188). The class, identified from publicly available antimalarial screening data, was optimised to generate early lead compounds that possess potent antimalarial activity against *P. falciparum* parasites comparable to the known antimalarials, chloroquine and mefloquine. During the optimisation process, we defined the functionality necessary for activity and improved *in vitro* metabolism and solubility. The resultant lead compounds possess potent activity against a multidrug resistant strain of *P. falciparum* and arrest parasites at the early phase of the asexual stage and also gametocytogenesis. We finally show that the lead compounds are orally efficacious in a 4 day murine models of malaria disease burden. Efforts towards target identification using affinity binding probes and resistance studies will also be discussed.

Optimising Manufacture of ^{68}GaRadiopharmaceuticals: Experience from a Clinical PET Service

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Positron emission tomography (PET) imaging is routinely used for clinical diagnosis and increasingly for medical research since quantification and visualisation of physiological processes may occur in real time. The development and use of Ga-68 radiopharmaceuticals is a growing area since the generator (68Ge/68Ga) based radioisotope allows more ready access, compared to other radioisotopes which are restricted to cyclotron or reactor production.

Radiolabelling data from an automated manufacturing process (Scintomics GRP® Synthesiser) will be presented for a selection of Ga-68 radiopharmaceuticals. These manufacturing processes have been optimised to achieve greater product activity per batch. This has particular benefits in a clinical setting, not only for process economics but more importantly increasing patient throughput for quicker access to diagnostic imaging services. The produced radiopharmaceuticals were assessed extensively by quality control criteria aligned with monograph regulations for related Ga-68 radiopharmaceuticals. This includes HPLC testing to quantify the reaction buffer which is identified as an impurity in monograph and subsequently determines the V_{max} for each batch released for clinical use. Further development and optimisation of these processes to produce high yielding, high quality and reliable supply of sterile injectable Ga-68 radiopharmaceuticals is a goal of this laboratory.

Oral delivery of folate targeted colorectal cancer therapeutics

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Colorectal cancer (CRC) is the third leading cause of cancer related mortality after lung and prostate cancer. Every year approximately 700,000 people die of colorectal cancer. Chemotherapy is typically administered by intravenous injection and infusion which often fails to deliver an effective concentration of the drug at the target site, with severe side-effects occurring due to off-target delivery (Prabhu et al., 2015).

Oral chemotherapy has the potential to open a new treatment concept called "chemotherapy at home". Unfortunately, most anticancer drugs are not suitable for oral delivery due to the myriad of physiological barriers as well as the physicochemical properties of the drugs (Saneja, 2014). The aim of this project is to develop a model carrier for oral delivery of colon targeted anticancer therapeutics that incorporates drug-encapsulated nanoparticles within microcapsules suitable for oral delivery.

An amphiphilic block copolymer of PEGMA-PMMA was synthesised and characterised successfully. Curcumin loaded micelles were formed having sizes of 30 and 70 nm with excellent drug encapsulation efficiency of 85.11% and 87.64%. Further, the micelles were encapsulated into an alginate microcapsule carrier to make a favourable formulation for oral delivery. *In vitro* release studies of the curcumin-loaded micelles showed a sustained diffusional release at pH 5.0 and 7.4.Cytotoxicity of the Curcumin loaded micelle and blank micelle were investigated. Biodistribution of microcapsules through oral delivery were investigated using small animal fluorescence imaging.

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Ordered Mesoporous Carbon Confined Gold Nanocatalyst

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ABSTRACT TEXT

Gold nanocatalysts represent a new generation of catalysts for the reduction of nitroarenes to aminoarenes using H_2. However, activated carbon has been seldom used for gold deposition due to the facts that traditionally used methods for metal catalysts are unfeasible for gold nanoparticles.[1] Here a coordination-assisted self-assembly approach is adopted for the intercalation of monodispersed gold nanoparticles inside ordered mesoporous carbon frameworks.

An almost complete conversion of benzyl alcohol to benzoic acid is achieved within 60 min over the 9 nm-Au/C catalyst under 90 ºC and 1 MPa, using potassium hydroxide as a base.[2] A reduction of gold particle size from 9 to 3.4 nm in the catalyst leads to a high activity toward the selective oxidation of benzyl alcohol to benzyl acid and toward the reduction of *p*-nitrophenol to *p*-aminophenol at a low temperature of 0 °C.[3] The electronic modification of the *d*-orbitals of small particles is extremely important for chemisorption of O_2 at atmosphere pressure and low temperatures.

Thermally reduced 2.8 nm Au nanocatalysts were highly active and selective, reaching an initial reaction rate of 12.7 and 6.5 min^{-1} to convert *p*-CNB and 4-NP using H_2 as a reducing agent, respectively.[4] Trapping by the SH-functionalized SBA-15 solids confirmed the negligible gold leaching and the heterogeneous active centers. The simultaneous thermal reduction of gold nanoparticles and pyrolysis of the matrix may facilitate the involvement of gold inside the carbon matrix, the modification of carbon atoms on the gold surface, and the reconstruction of the surface induced by CO adsorption. The generation of low-coordinated gold atoms possibly reduces the H_2 dissociation barrier, and can therefore significantly improve the hydrogenation activity. In addition, the encapsulation of gold nanoparticles inside carbon matrix enhances the stability.

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Organosilica nanoparticles as scaffolds for reversible biosensors

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Despite rapid advances in the design of nanoparticles for therapeutic purposes, the related field of "nanosensors" for applications in biological environments has not advanced at the same rate. While there are many research groups independently developing new scaffold materials and biological receptors that could be applied in this area, only a handful of groups have demonstrated *in vivo* sensing (as opposed to labelling) in live animal models. The ion-selective "optodes" developed by Clark's group have undergone the most comprehensive testing to date, demonstrating real-time monitoring of a range of physiological biomarkers and metabolites. They have also shown the utility of pH-selective optodes for sensing small molecules including glucose using encapsulated enzymes. However, these materials are prone to reagent leakage *in vivo*, currently limiting their operating lifetime.

We are investigating the potential of core-shell organosilica nanoparticles as material scaffolds for *in vivo* nanosensing applications. The key advantages of this material include simple control over particle core size (0.05-5μm; <10% standard deviation), shell porosity (via choice of base or porogen) and chemical functionality (range of functionalised silane monomers available). Colloidal stability of the nanoparticles can easily be maintained for days in culture media by incorporation of silane-functionalised PEGs or anti-fouling peptides. Here we will present our latest results on how the key material properties (shell thickness, porosity, polymer coatings) affect the analytical characteristics (dynamic range, reversibility, response time) of a pH nanosensor in aqueous solutions.

ORIENTATION AND SURFACE DYNAMICS OF ORGANIC ADSORBATES ON AMORPHOUS SILICA

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ABSTRACT TEXT

Details of adsorption dynamics and preferred orientation of molecules on surfaces are important for understanding heterogeneous catalysis. In this talk, I will show how quantum chemical calculations and molecular dynamics simulations are paired with sum frequency generation spectroscopy to elucidate the orientational preferences, rotational dynamics and adsorption thermodynamics of α-pinene molecules on amorphous silica. Specifically, classical molecular dynamics simulations predict that there are two populations of α-pinene molecules on silica that are characterised by very different rotational relaxation times. This prediction is supported by very recent experiments that provide evidence for tight and loose physisorbed states of α-pinene molecules bound to silica. The origin of these adsorption states are investigated, and our findings are expected to have direct implications on the conversion of terpenes over silica-based catalysts.

OUTCOMES OF THE TERTIARY CHEMISTRY PEDAGOGICAL CONTENT KNOWLEDGE PROJECT

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ABSTRACT TEXT

Elements of tertiary pedagogical content knowledge (PCK) have been collected through engagement with the community of chemistry academics through a series of workshops around Australia. In parallel with these workshops, ten structured interviews were conducted with expert tertiary chemistry teachers with different sub-disciplinary specialisations. The combined data has been analysed to evaluate alignment with the consensus model for professional knowledge and skills that has evolved from the secondary level. In-depth textual analysis of the interview transcripts has revealed aspects of tertiary PCK that are linked to sub-disciplinary differences in approaches to teaching chemistry. However, overall alignment was evident among the approaches of expert teachers including the use of active learning and student-centred strategies and the choice of humanistic examples to illustrate their teaching. Other persistent themes included knowing students' backgrounds and trajectories, and a focus on concepts rather than rehearsal of algorithmic calculations. Strategies for teaching practice will be presented, including what does not work, and recommendations for how transferable PCK can be used to accelerate our growth as teachers, particulary in fields outside our own subdisciplinary expertise.

OXIDATIVE ADDITION OF EPOXIDES TO NICKEL(0) WITH RETENTION OF CONFIGURATION

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2-Nickelaoxetanes have been invoked as reactive intermediates in several catalytic olefin oxidation reactions, yet only a few 2-nickelaoxetanes have been isolated and characterized. Proposed catalytic reaction mechanisms invoke the formation of a 2-nickelaoxetane intermediate from Ni(0) and an epoxide by an S_N2 mechanism followed by ring closure. Building on our studies of rhodaoxetanes and related heterocycles, we have recently been focused on the synthesis and reactivity of well-defined nickelaoxetanes. We have discovered that ketones are effective directing groups for the oxidative addition of Ni complexes with epoxides to give rare examples of isolable, well-defined 2-nickelaoxetanes with retention of configuration. Deuterium-labelling studies and DFT calculations support a concerted oxidative addition of the C-O bond, rather than S_N2-type attack, to form the nickelaoxetanes. Very recently, we have shown that a directing group is not needed to promote ring-opening of epoxides with retention of configuration. We are analysing the differences between our Ni complexes, which react with retention, and those from previous reports, which react with inversion. We anticipate that this study will lead to new reactivity of the resultant nickela(II)oxetanes.

Oxygen Tolerant Polymerisations for the Combinatorial Design of Biomaterials

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High throughput combinatorial synthesis of polymers is emerging as an important method for the discovery and development of novel biomaterials. By rapidly screening libraries of polymer structures, promising candidates can often be much more reliably found than by a rational design approach. [1]

We recently developed a method for preparing well-defined polymers in the presence of oxygen, which makes use of the enzyme glucose oxidase to scrub oxygen from reversible addition fragmentation chain transfer (RAFT) polymerizations, which we termed Enz-RAFT.[2,3] Since our work a number of other approaches have been demonstrated which make use of photocatalysts such as eosin Y,[4] and porphorins[5] to scrub the oxygen. Using such systems, polymerizations can be conducted in extremely low volumes (<40 μL) without any degassing in microtiter plates across a range of monomer families and molecular weights. Block extensions can be performed in a single well without any purification by simple addition of the subsequent monomer, and complex star polymers can be prepared either *via* polymerization from multi-arm RAFT agents or *via* an arm first approach. Recent results on the architectures available from oxygen tolerant well plate polymerizations and our application of these systems to design novel biomaterials will be discussed.

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Paper-based nanosensor for the rapid screening of drug metabolites

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ABSTRACT

An ultra-sensitive substrate for the detection of drug metabolites in biological fluids has been developed by depositing gold nanostructures onto A4 paper. The paper-based substrate was used for surface enhanced Raman spectroscopy (SERS) to detect and quantify the sofosbuvir metabolite, 2'-deoxy-2'-fluoro-2'-C-methyluridine (PSI-6206) in blood plasma by HPLC-SERS. The limit of quantification for PSI-6206 using the SERS detection was found to be 13 ng L^{-1} (R^2 value = 0.959, RSD =5.23%). The new HPLC-SERS method was compared to HPLCDAD and HPLC-MS methods and found to be more sensitive than the HPC-DADA by 4 orders of magnitude while providing unique structural identification of the analyte, similar to Mass spectroscopy. Due to the disposable nature of the paper-based sensor, the new HPLC-SERS method does not suffer from the memory effect that exists in traditional HPLC-SERS methods and cause false positive identification of analytes. The paper-based HPLC-SERS has strong potential as a sensitive and cost effective platform for the determination of drug metabolites in biological fluids by Raman spectroscopy.

Pd(I) catalysed oxidative cross-coupling of aryl and heteroaryl nucleophiles

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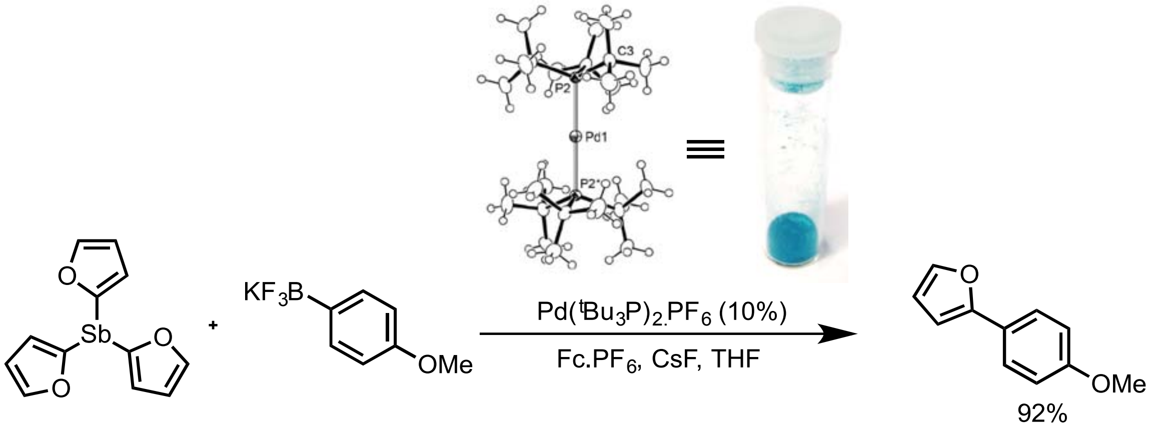
Palladium-catalysed cross coupling chemistry is typically understood to proceed via a series of two electron processes (oxidative addition, reductive elimination). The recent rise of single electron transfers in transition metal catalysed cross coupling has opened up new coupling strategies, but has largely been focused on nickel and copper.[5]

Making use of a recently reported monomeric palladium(I) species,[6] we will present a selective, oxidative cross coupling between aryl-metal nucleophiles (M = B, Sb, Bi ect). The scope of this reaction and initial mechanistic studies will be discussed, along with the potential use of palladium(I) in future reaction design.



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PdCu@Pd Nanocube with Pt-like Activity for Hydrogen Evolution Reaction

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ABSTRACT TEXT

The electronic properties of metal surfaces can be modulated to weaken the binding energy of adsorbed H-intermediates on the catalyst surface, thus enhancing catalytic activity for the hydrogen evolution reaction (HER). Here we first prepare PdCu alloy nanocubes (NCs) by coreduction of $Cu(acac)_2$ (acac = acetylacetonate) and Na_2PdCl_4 in the presence of oleylamine (OAm) and trioctylphosphine (TOP). The PdCu NC coated glassy carbon electrode is then anodized at a constant potential of 0.51 V vs Ag/AgCl at room temperature in 0.5 M H_2SO4 solution for 10 s, which converts PdCu NCs into core@shell PdCu@Pd NCs that show much enhanced Pt-like activity for the HER and much more robust durability. The improvements in surface property and HER activity are rationalized based on strain and ligand effects that enhance the activity of the edge-exposed Pd atoms on core@shell PdCu@Pd structure. This work opens up a new perspective for simultaneously reducing metal Pd cost and achieving excellent performance toward the HER.

Pentacene End-Labelled Polymers for Self-Assembly Driven Singlet Fission

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Singlet exciton fission is a photophysical process that can produce multiple spin-triplet excitons following a single photon absorption event. While renewed interest in the field has been fuelled by the prospect of increasing single junction photovoltaic efficiencies beyond the Shockley-Queisser limit, the utilization of singlet fission in other photonic applications has received comparatively less attention, in-part due to the limited number of singlet fission systems reported to-date.

In this presentation, the results of our recent investigation into singlet fission in solution-based assemblies of TIPS-pentacene labelled DNA and ethylene glycol polymers will be discussed. End-labelled polymers of each were synthesized using copper(I)-catalyzed azide-alkyne cycloaddition 'click' chemistry between an alkyne-functionalized TIPS-pentacene precursor and the corresponding azide-terminated polymer. All polymers form micelles in aqueous solution that undergo singlet fission at the pentacene-rich core, as revealed by ultrafast transient absorption experiments. We find that the singlet fission dynamics and triplet yield are governed by differences in local interchromophore contacts within the micelle core, with the di-functionalized polymers displaying the most rapid single fission. Intriguingly, singlet fission is observed in a fully solvated di-functionalized hairpin DNA oligomer in THF solution, creating the possibility of using DNA to assemble molecular dimers capable of efficient solution-based singlet fission. This work demonstrates the potential of using end-labelled polymers to drive the formation of nanostructures conducive for singlet fission, providing scope for the development of hierarchical systems utilizing this fascinating phenomenon.

PEO-based brush-type amphiphilic macro-RAFT agents and their assembled monolithic structures

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Polymerized High Internal Phase Emulsions (PolyHIPEs) were prepared using emulsion-templating, stabilized by an amphiphilic diblock copolymer prepared by reversible addition fragmentation chain transfer (RAFT) polymerization. The diblock copolymer consisted of a hydrophilic poly(ethylene glycol) methyl ether acrylate (P(PEO MA), average Mn 480) segment and a hydrophobic styrene segment, with a trithiocarbonate end-group. These diblock copolymers were the sole emulsifiers used in stabilizing "inverse" (oil-in-water) high internal phase emulsion templates, which upon polymerization resulted in a PolyHIPE exhibiting a highly interconnected monolithic structure. The polyHIPEs were characterized by FTIR spectroscopy, BET surface area measurements, SEM, SEM-EDX, and TGA. These materials were subsequently investigated as stationary phase for high pressure liquid chromatography via in situ polymerization in a capillary format as a 'column housing'. Initial separation assessments in reversed-phase (RP) and hydrophilic interaction liquid chromatographic (HILIC) modes have shown that these polyHIPEs are decorated with different microenvironments amongst the voids or domains of the monolithic structure. Chromatographic results suggested the existence of RP/HILIC mixed mode with promising performance for the separation of small molecules.

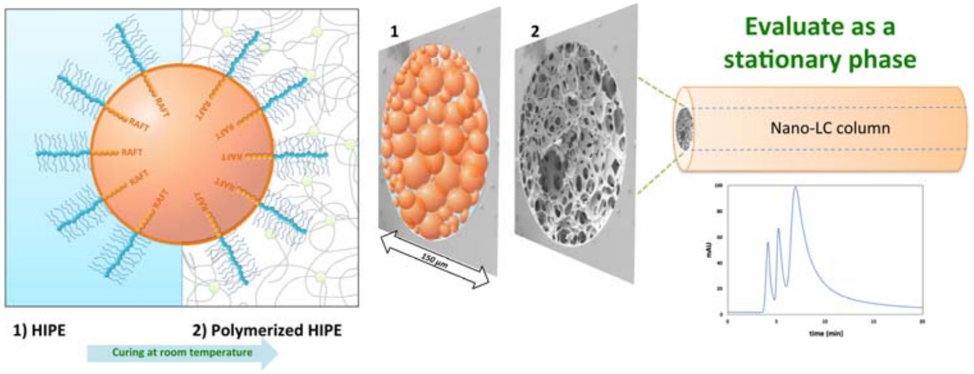

Figure 1. Mechanism of polyHIPE surface functionalization. 1) HIPEs stabilized by PEO-based brush-type amphiphilic macro-RAFT agents as surfactants 2) By *in situ* polymerization of the continuous phase, these amphiphilic species can be surface functionalized through PEO brush-type block (physical or chemical) entanglement.

PET-RAFT Technique for Sequence Control in Polymer Synthesis

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The ability of plants to convert solar energy into chemical energy via photoredox processes (natural photosynthesis) has inspired generations of chemists to try to reproduce such systems. Recently, the use of visible light photoredox catalysis in organic chemistry has enabled the synthesis of known chemical compounds through novel synthetic routes, limiting the formation of side products and eliminating complex purification procedures.[1] In addition to the high efficiency of these reactions, which require catalyst concentrations in ppm amounts, a number of photoredox catalysts have demonstrated additional remarkable properties, including compatibility and selectivity. Taking advantage of its compatibility with a number of common catalytic processes, recent development in the field of visible light photocatalysis has been dedicated to merging various catalysts to perform complex organic transformation in a single pot.

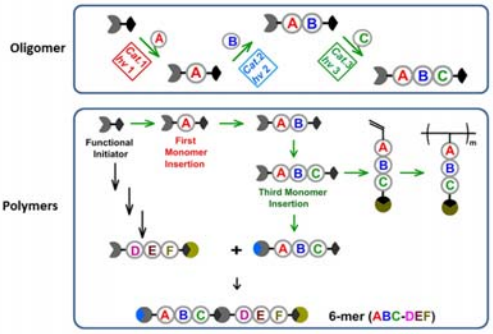

Figure 1. The construction of sequence-defined oligomer and polymers

More recently, the successful implementation of photoredox catalysis in polymer chemistry has led to the development of novel light mediated polymerizations, in living polymerizations.[2] We have developed a living radical polymerization technique involving the reversible deactivation of thiocarbonylthio compounds by photoredox catalysts via a photoinduced electron/energy transfer (PET) process. Recently, we reported the first exploitation of selective activation of trithiocarbonates in the presence of zinc tetraphenylporphine (ZnTPP), leading to the fast and controlled polymerization of acrylates, even under open air conditions.[2e]

In this abstract, we employ the unique property of selective activation for controlled radical polymerizations,[3] specifically PET-RAFT polymerization, to produce sequence-defined polymers (**Figure 1**) through the approach of single unit monomer insertion to RAFT agents.[4]

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pH Responsive Nanoparticles for Probing Cellular Behaviour

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The use of nanoparticles for drug delivery has received wide spread attention in recent years. Soft nanoparticle carriers have the potential to improve therapeutic outcomes compared to therapeutics alone due to their more targeted drug release, thus reducing negative side effects. However, there is still limited understanding of the kinetics of nanoparticle disassembly in a cell and thus cargo release. One technique used to probe the cellular behaviour of nanoparticles is the use of fluorescent sensors, which change fluorescent behaviour based on cellular changes. Herein we report the design of pH responsive polymer biosensors with capability to conjugate to two different fluorescent dyes (cyanine 3 (cy 3) & sulfo-cyanine 5 (sulfycy5)). The nanoparticles were formed by the nanoprecipitation of two pH-responsive polymers. The shell component is poly (ethylene glycol)-b-poly((2-(diethylamino)ethyl methacrylate)-r- pentafluorophenol methacrylate) (PEG-b-(PDEAEMA-r-PDPAEMA)), which is labeled with sulfycy5. The core component is a random copolymer poly(2- (diethylamino) ethyl methacrylate)-r-poly (2-(diisopropylamino) ethyl methacrylate)-r-pentafluorophenol methacrylate (PDEAEMA-r-PDPAEMA-r-PFPMA), which is labeled with cy3. These particles are stable in the pH of the blood-stream (approximately pH 7.4) but disassemble in acidic pH of the intracellular vesicles (endososomal/lysosomal compartments). This change from a particle to a unimer should lead to different fluorescent properties and thus makes them suitable for use as a biosensor to study pH variation in a cell. The fluorescence characteristics of these particles were investigated with dyes incorporated in the core, shell and a combination. It was observed that these particles had different fluorescence behaviour at pH 8 (particle) and pH 6 (disassembled form) as expected. Interestingly, the number of dye molecules per polymer was found to change the ratio of fluorescence at pH 6/pH 8. The position and type of dye also had an effect on fluorescent behaviour. These insights are important for the design of biosensors with optimised fluorescent readout in the cell.

Photo-degradation of Enrofloxacin and Gatifloxacin under UV and Simulated Sunlight

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Substantial concentrations of fluoroquinolone antibiotics are found in the lakes and rivers in China. Enrofloxacin (ENR) and gatifloxacin (GAT) were selected to represent fluoroquinolone antibiotics in this study to understand the controlling factors on the photo-degradation of these antibiotics in aqueous solutions under simulated sunlight and UV light. An Agilent 1260 HPLC-DAD was utilized to determine the concentrations of ENR and GAT. Experimental results demonstrated that the photo-degradation of ENR and GAT followed first order reaction kinetics, and factors such as solution initial pH, hydrogen peroxide, nitrate, humic acid and rose bengal could affect the photo-degradation. The rate of degradation was faster under ultraviolet light rather than simulated sunlight, and GAT barely underwent degradation under simulated sunlight. Mixed solutions of ENR and GAT were exposed to UV light and their rates of photo-degradation were 44% and 6.1% lower in comparison with their respective rates in solutions of single antibiotics. It appeared that singlet oxygen ($^1O_2$) and hydroxyl free radical ($\cdot OH$) participated in the degradation through photosensitization. Initial pH of the aqueous solution also influenced the degradation rates of ENR and GAT, the rates seemed to increase with increasing pH initially but declined after reaching a maximum. At the optimal pH of 7, 69.8% of the ENR and 44.7% of GAT in the solutions underwent photo-degradation. Hydrogen peroxide, nitrate anions and dissolved humic acid tended to enhance the photo-degradation of ENR and GAT. Rose bengal at a concentration of 10 μM was showed to enhance the degradation of ENR and GAT.

Photodissociation action spectroscopy of protonated N-containing aromatic ions: can we predict photodissociation pathways?

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ABSTRACT TEXT

Nitrogen containing aromatics are fundamental building blocks of many biomolecules, charge-transfer dyes, ionic liquids and fluorescent tags. Despite their ubiquity, there is a lack of spectroscopic data – particularly for their protonated variants – that provide details about their excited-state structure, stability and fate. These details are vital to support models of light-activated biochemistry involving proton-transfer, electron-transfer and internal conversation. Generally, modelling excited-state processes is a tricky business and therefore experimental data are vital to guide the construction of sound models and computational tools.

We use a combination of ion-trap mass spectrometry and tunable UV-Vis pulsed laser radiation to detect and measure the wavelength-dependet generation of photoproducts. Computational results for excited-states and ground state photodissociation pathways assist in assigning the spectra

In recent results, we have examined the action spectroscopy of N-protonated ethynylpyridinium ions (ortho, meta and para) for the first time to examine how electron-rich substituents on pyridinium ion affect the photodissociation pathways and state-energy of the excited states. UV photodissociation spectra are measured - which in some case exhibit vibronic detail - and multiple photodissociation channels are detected.

For these ethynylpyridinium ions, photodissociation pathways lead to either retention of the N atom in the ring (from C_2H_2 elimination) or its expulsion (with HCN elimination) - and its not clear at this stage what mediates the photodissociation. Are there common intermediate states? Our group is trying to rationalise some guiding principles to understand and predict photodissociation of protonated N-containing aromatics.

PHOTOPHYSICALLY ACTIVE GRAPHENES

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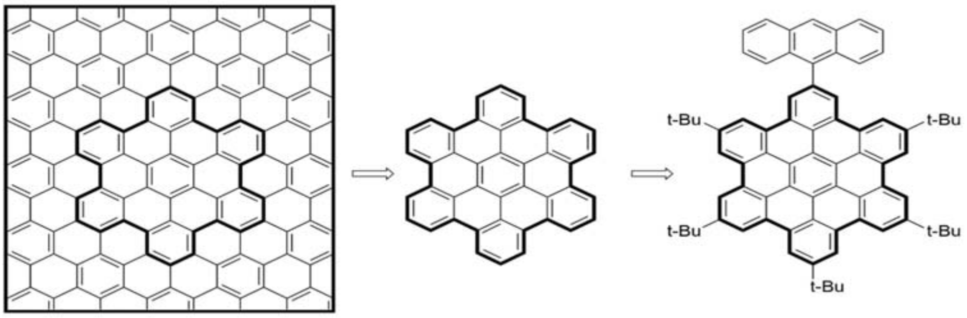
The investigation of graphene (**1**), a discrete two-dimensional graphite fragment, continues as a prominent research area since it was isolated in high yield in 2004.[1] Due to extended conjugation and charge carrying properties graphene has many potential applications, particularly as the active element in molecular devices in the field of organic electronics. Current methods to produce graphene usually involve top-down strategies producing mixtures of graphenes with poorly defined shape and size, thus, varied properties. The properties of graphenes are directly dependant on their structure, controlling this becomes crucial for future applications. Ultimately, atomic level control of graphene structure and therefore their properties can only be achieved through advanced organic synthetic techniques.[2]

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds that represents well-defined nano-graphenes. The synthesis of PAHs can be utterly controlled giving rise to pure samples of a single graphene for further study. The research described involves the synthesis of PAHs based on hexa-*peri*-hexabenzocoronene (HBC, **2**) that contain smaller aromatic molecules attached at the periphery. These molecules can act as chromophores, and we aim to investigate the effects on the photophysical properties with a focus on future applications, particularly as functional elements in OLEDs. Another property which limits their application is their low solubility which can be altered during synthesis with minimal impact on the photophysics.



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PHOTOVOLTAIC APPLICATION OF PORPHYRIN PROTEIN MAQUETTE-BASED REACTION CENTRES

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The emulation of photosynthesis, the efficient and sustainable utilization of solar energy using renewable materials to produce hydrogen and oxygen from water or convert carbon dioxide into a chemical feedstock represents one of the great scientific challenges of the 21st Century. Creating photosynthetic-like processes in devices could not only provide a new generation of economical photovoltaic devices but also lead to sustainable hydrogen production through water splitting as well as fuel and food production through carbon dioxide fixation.

In 1994, Dutton and his co-workers developed the methodology for the facile production of de novo synthetic protein helices (maquettes), structurally simpler analogs of natural redox proteins, which have proved extremely useful for the study of porphyrin behaviour and interactions in proteins. It has been demonstrated that not only is a maquette bound porphyrin more efficiently photo oxidized than a free porphyrin but also that light induced electron transfer between the porphyrin complex and an acceptor is faster and higher yielding. As the maquettes can be assembled on a variety of surfaces such as gold or titanium dioxide, they provide a unique platform on which to build and study a light harvesting reaction center replica.

We have incorporated carboxylated porphyrins into maquettes and bound these artificial reaction centres to titanium dioxide in a dye sensitized solar cell (DSSC) to create the first artificial protein based dye sensitized solar cells. In this paper, we will discuss the development of these artificial reaction centres and the characteristics of the resulting photovoltaic devices.

pH-Switchable Electrostatic Catalysis

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ABSTRACT TEXT

Normally it is thought that electric fields can only be used to accelerate redox reactions; however, it should also be possible to catalyse non-electrochemical reactions by electrostatically stabilizing higher energy charge-separated resonance contributors of the transition state. In practice, the problem is orienting the field relative to the reaction centre. Recently we showed that this can be done using scanning tunnelling microscopy and surface chemistry techniques (Aragones et al. *Nature* 2016), but this is not really feasible in a bulk solution-phase chemical process. An alternative approach is to utilise charged functional groups within the substrate, auxiliary or catalyst whose electric field is relatively localised but can be precisely oriented relative to the reaction centre. If the charged functional group is an acid/base group, this also has the advantage of incorporating a pH-switch to the catalytic effects. Recently, we have provided proof-of-concept for pH-dependent electrostatic catalysis by demonstrating a pH-switch of up to two orders of magnitude on the rate and equilibrium constant for hydrogen atom transfer between a hydroxyl amine bearing a non-conjugated carboxylic acid and a reference profluorescent nitroxide radical (Klinksa et al. *Chem Sci.* 2015). Deprotonation of the carboxylic acid stabilizes the resulting nitroxide radical anion, favouring the forward reaction. We are now looking to generalise this approach in organocatalysis, where it should be possible to manipulate stereo- and regioselectivity with pH-switchable electrostatic effects. This presentation will outline our progress towards harnessing these electrostatic effects in chemical and polymer synthesis.

Plasmonic endoscopy toward single cell interrogation

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ABSTRACT TEXT

Metal nanowires act as plascmonic wave-guides, allowing to confine and transfer light energy over many micrometer distance below sub-diffraction limited dimension. Plasmons confined at the surface of single metal nanowires, such as wet-chemically synthesized silver/gold nanowires, can propagate over tens of microns before energy is lost by Ohmic damping. Alternatively, the use of surface plasmons allows us to concentrate light energy in nanometer regions, leading to a massive enhancement of electromagnetic filed that can be used for surface enhanced Raman scattering (SERS) or fluorescence (SEF) spectroscopy/microscopy.

In this talk, I will introduce a noble nanoscopic techniques using a combination of these two concept, that of surface enhanced Raman scattering (SERS) and surface enhanced fluorescence of (bio)molecules and that of sub-diffraction limit plasmonic waveguiding. Specifically, we demonstrate that propagating plasmons launched along a silver nanowire (50 ~ 100 nm diameter) can remotely excite SERS [1,2] and SEF [3] in the vicinity of the nanowire surface due to the SPPs wave-guiding effect. The ability to transfer SERS/SEF excitation over several microns, through sub-diffraction limited structures, will be discussed with respect to potential application toward super-resolution endoscopy [4] and tip-enhanced Raman microscopy [5].

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Plasmonically enhanced photocatalytic hydrogen evolution with TiO_2/TiN nanoparticle composites

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The development of efficient, robust and scalable photocatalysts for solar hydrogen evolution is an attractive approach for future energy demands.[1] Transition metal oxides have been extensively investigated due to their robustness, scalability, and in the case of TiO_2, adequate band edge positions. Such metal oxides typically have large band gaps (utilising < 5% solar spectrum) while also suffering from charge carrier recombination. Strategies such as addition of noble metal co-catalysts (Pt, Au, Ag) and/or visible light sensitisation have been employed to dramatically increase activity by reducing electron/hole recombination rates;[2] and to utilise more of the solar spectrum. However, the high cost of noble metals reduces their potential industrial scale application.

Transition metal nitrides have emerged as attractive materials for photocatalytic applications due to their low cost, high melting points (TiN m.p. = 2950 °C), thermal and electrical conductivity, tuneable stoichiometry, and the ability to harvest visible light *via* surface plasmon resonance. We have investigated the application of TiN nanoparticles to enhance the H_2 evolution activity of a TiO_2 photocatalyst (P25). We report here our recent results of the preparation, characterisation and application of TiO_2/TiN nanoparticle composites for H_2 evolution. Two different samples of TiN, prepared by plasma techniques, were employed to investigate the effect of different morphologies and properties. A 3-fold increase in activity for TiO_2/TiN compared to bare TiO_2 was observed. Combined UV/Vis irradiation is necessary for enhanced activity, compared to UV only, indicating that the surface plasmon of TiN contributes to the enhanced activity of the TiO_2/TiN composite.

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PLGA Microsphere/P(NIPAAm-*co*-AAm) Hydrogel Combination systems for drug Delivery

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A combination system with incorporating poly(lactic-co-glycolic acid) (PLGA) microspheres into porous P(NIPAAm-co-AAm) hydrogel was developed for sustained delivery of drug The interior morphology and the structure of PLGA microspheres/P(NIPAAm-co-AAm) hydrogels combination systems was determined by SEM and FTIR, respectively. The swelling/deswelling properties and drug release manner of combination system were investigated by dynamic evaluation methods in vitro. FTIR results exhibited that PLGA microspheres were incorporated physically into temperature sensitive P(NIPAAm-co-AAm) hydrogel to form the combination system. The SEM results showed that PLGA microspheres were encased into the interconnected porous structure of P(NIPAAm-co-AAm) hydrogel and the interconnecting and the pore size of the porous structure decreased. The amount of PLGA microspheres incorporated had no significant impact on the LCST of the combination systems, and all combination systems have almost the same LCST at about 37 oC. But the swelling and deswelling rate of the combination systems decreased with increasing the amount of incorporated PLGA microspheres. In vitro release of BSA from combination system exhibited a low burst release followed by a slow sustained release for 30 days as compared to BSA release from the PLGA microspheres and P(NIPAAm-co-AAm) hydrogels alone. The release of BSA from combination systems was better controlled when compared to delivery from hydrogels and microspheres alone. The combination systems showed great promise for application in drug delivery systems.

Poly(acryloylhydrazide) as a versatile scaffold to synthesise polymers for biomedicine

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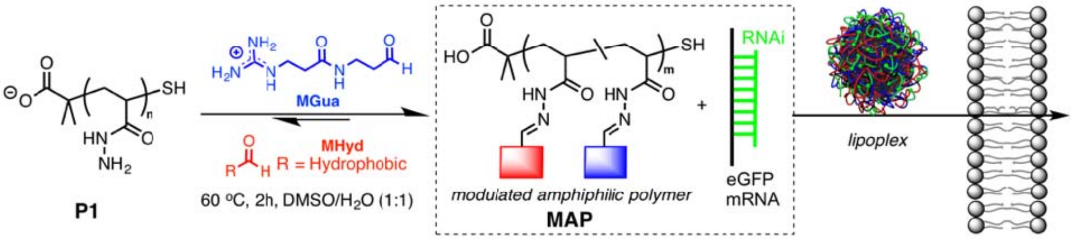
Here we present the synthesis and post-polymerisation of poly(acryloyl hydrazide), a versatile scaffold for the preparation of functional polymers. Our synthetic approach includes the synthesis of a Boc-protected acryloylhydrazide, the preparation of polymers via RAFT polymerisation and the deprotection of the corresponding Boc-protected poly(acryloyl hydrazide). Post-polymerisation of poly(acryloyl hydrazide) is demonstrated using a range of conditions for both hydrophilic and hydrophobic aldehydes. We explore the potential of this strategy by synthesising and in situ screening polymeric amphiphiles for the delivery of small interfering RNA (siRNA). The activity of the formed polymeric amphiphiles can be evaluated using both model membranes and model cell lines, without the need for isolation and purification of the polymers. This method constitutes an improved alternative to current screening methods and can underpin the discovery of new functional polymers with complex chemical functionality.



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Polydiacetylene-(phen)Ru(bpy)$_2$/Rh catalyst for Cofactor Regeneration and CO$_2$ Reduction as An Artificial Photocatalytic System

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ABSTRACT TEXT

For the practical use of a photo-bioreactor for artificial photosynthesis, efficient visible light-absorbing materials have to link reduction and oxidation catalysts for an efficient energy flow. As a step toward this goal of an NADH regeneration system and enzymatic production of solar fuels from CO_2, we report the synthesis of a new polydiacetylene compound that is covalently connected with $[Ru(phen\text{-}NH_2)(bpy)_2]^{2+}$ (bpy = 2,2’-bipyridine, phen = 1,10-phenonthroline-5-amine). The $[(bpy)_2Ru(phen)]$-polydiacetylene absorbed a wide range of visible light because of the presence of two chromophores, the Ru complex and polydiacetylene. The polyacetylene backbone was converted from blue to red by conformational changes under the catalytic reaction conditions in a buffer solution. The electron transfer from the photoexcited $[Ru(phen)(bpy)_2]^{2+}$ to the polydiacetylene backbone was observed. In a visible light-driven photocatalytic NAD$^+$ reduction by (cyclopentadienyl)Rh(bpy)$(H_2O)^{2+}$ with $[(bpy)_2Ru(phen)]$-polydiacetylene, NADH was regenerated, and the reactivity using Ru(bpy)$_2$(phen)-polydiacetylene was enhanced relative to control experiments using only $[Ru(phen)(bpy)_2]^{2+}$ or polydiacetylene. The consecutive carbon dioxide reduction coupled with formate dehydrogenase was carried out to utilize the in-situ photoregenerated NADH catalytically. The catalytic condition using $[(bpy)_2Ru(phen)]$-polydiacetylene also showed much higher reactivity than the controls.

Polymer Brushes: Synthesis, Self-assembly and Applications

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ABSTRACT TEXT

Brush-like macromolecules, possessing multiple side chains attached onto a backbone, are endowed with some unusual properties, including a wormlike conformation, notable chain end effects and compact molecular dimension resulting from their confined and compact structure, compared with the corresponding linear macromolecules with the same molecular weight.[1] Continuously increasing attention has been paid to these interesting macromolecules due to their importance in understanding the relationship of architectures with properties and their potential applications such as drug and gene delivery system, synthesis of nanostructure and preparation of hybrid nanostructure.[1] Moreover, compared with linear amphiphilic and double hydrophilic block copolymers, the corresponding graft copolymers not only have some unique micellar behaviors, but also their self-assemble behaviors can be easily varied by simply adjusting the graft densities and the chain lengths of the side chains. We had developed a variety of efficient strategies to prepare a series of functional polymer brushes and examine their multiple stimuli-responsive self-assembled behaviors.[2-5] In addition, those functional polymer brushes showed promising applications in anti-fouling surface and smart drug delivery carriers.[6-8]

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Polythiophene Phenylene Derivatives With Added Functionalities

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Functionalisation of conducting polymers is an important area of research in the interest of increasing the processability of the material and bestowing additional properties. We have previously shown that polythiophene phenylenes (PThPs) allow a wide range of functionalities to be easily incorporated in its structure. This includes side chains that can undergo pre- or post-polymerisation modification using Atom transfer radical polymerisation (ATRP) grafting and through azide-alkyne Huisgen cycloaddition 'click' chemistry.[1] ATRP can be used to graft copolymers to the conducting PThP backbone, modifying the physical properties while still retaining the original electroactivity of the backbone. 'Click' chemistry enables the attachment of a wide range of compounds such as peptides and other biomolecules allowing the systems to be biocompatible and/or act as biosensors. We report on the synthesis and properties of highly functionalised PThPs; for example copolymer **1** (fig 1) which has been modified to be water soluble and displays thermoresponsive properties.

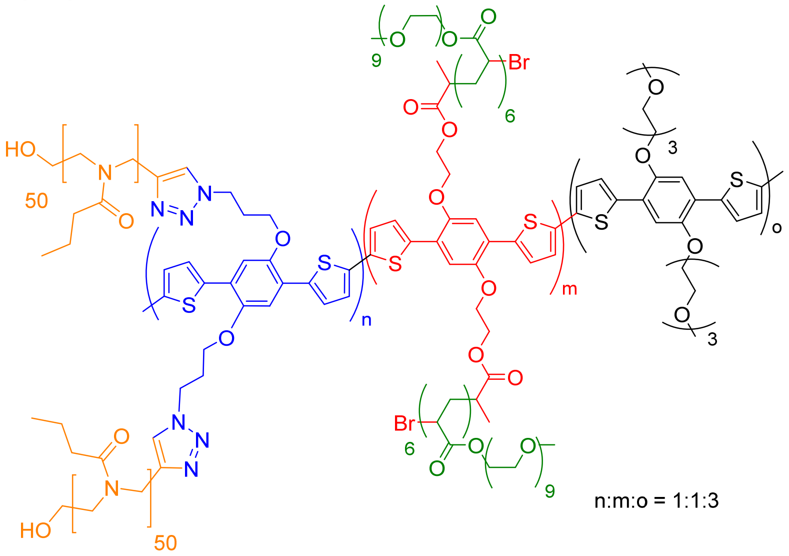

Figure 1. Highly functionalised, water soluble, thermoresponsive polythiophene phenylene copolymer

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Porous Chitosan/Hydroxyapatite Composite Membrane for Static and Dynamic Dye Removal from Aqueous Solution

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The unique characteristics of Chitosan (CS) such as resource abundance, good biocompatibility, film-forming ability and sufficient sites (–NH_2 and –OH) for adsorption of heavy metals or organic pollutants make CS-based membranes a promising membrane adsorbent. In this work, a porous Chitosan/Hydroxyapatite (CS/HA) membrane with a sponge-like surface and a three-dimensional interpenetrated porous structure of about mean pore size less than 10 μm was developed for dyes removal. The azo dyes of DB15 was chosen as a model dye. The most striking advantage of the proposed membrane lies on the integration of appreciably high adsorption capacity (as compared with current CS-based membranes, also 2.5 times and 4 times higher than that of non-porous CS/HA membrane and the commercially available activate carbon) and the high-speed dynamic dye removal (98% or even better in less than 15 min). Besides, the synthesis protocol for the proposed membrane is also much simpler, environmental-friendly and economical. Moreover, the proposed membrane also featured repeated dye removal (above 80% after 5 cycles of dynamic adsorption at dye concentration of 150 mg L^{-1}). All the above advantages indicated the intriguing potential of the porous membrane in practical wastewater treatment.

Potential Applications of Metal–Organic Frameworks in Microelectronics

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Metal–organic frameworks (MOFs) have emerged as a promising class of materials with a variety of applications. Since MOFs contain both inorganic and organic components, they have been extensively studied for applications in gas storage, chemical separation, sensing, catalysis, drug delivery and biomedical imaging. MOFs with a high porosity, good thermal stability and ease of tunability of their structures make them a suitable choice for use as electronic materials in the years to come. Nevertheless, efforts directed towards their use in microelectronic applications have been much less. We have been investigating fundamental dielectric, semiconducting and optical properties of various MOFs and have summarized current state of the initial theoretical and experimental research which promises to pave the way for further studies of MOFs with interesting potential applications in microelectronics.

PRECISION FUNCTIONAL POLYMERS BY PRECISION RADICAL POLYMERIZATION: PERSPECTIVE

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ABSTRACT

This lecture will focus on the recent development of transition metal-catalyzed living radical and related polymerizations for the precision synthesis of functional polymers. Following a brief overview of the status quo of catalyst and reaction design of the living polymerizations, discussion will be directed to a family of well-defined polymers of varying architectures and functionality. Specific examples will include: (a) statistically random amphiphilic copolymers that undergo unique “chain-folding” to form presumably spherical objects in water where a nano-scale space is constructed; (b) microgel “star” polymers that also generate larger nanospace for molecular recognition and selective encapsulation of substances for removal and/or storage; and (c) “sequence-controlled” macromolecules where selected functionalities are precisely placed along a relatively short carbon-based backbone. A particular focus will be directed toward the topic (c), i.e., sequence control in chain-growth polymerization, which the author and his group consider one of the most significant but challenging frontier in synthetic polymer science and chemistry. An intriguing question therefore: Why has nature not designed and produced carbon-based macromolecules of precision sequence after 13.5 billion years of its history?

PREDICTING PKA – BEYOND SMALL, RIGID MOLECULES

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ABSTRACT TEXT

Accurate pKa values are crucial for assigning protonation states of molecules in solution, and for assessing their susceptibility to proton transfer reactions. Whilst there is an abundance of experimental data in the literature, accurate measurements can be challenging or impossible for many systems, particularly metastable species and transition states. Hence, the development of accurate first principles methods for predicting pKa values is the subject of intense research activity. Much of this activity has focused on developing methods which can give accurate pKa predictions for small rigid molecules. However, many of the systems which are of greatest chemical or biochemical interest are neither small nor rigid. In order to make reliable pKa predictions for such species, it is critical to correctly identify the molecular conformation(s) which are adopted in solution. Here we examine various approaches to comparing conformational stabilities, and identify the factors which are important for making selections which give good pKa predictions. Factors include the metrics used to compare conformations (energy or free energy, gas phase or solution phase), the methodology used to calculate solution phase free energies (thermocycles or entirely solution phase calculations), the inclusion of explicit water molecules and the use of "quasi-harmonic oscillator" approximations to reduce errors due to poor prediction of low energy vibrational frequencies. We have been exploring these factors in the context of predicting pKa values for a series of cationic amines and polyamines. This presentation will outline our results and highlight some of the ongoing challenges in first principles pKa prediction.

Predicting the emission efficiency of light-emitting complexes in OLEDs

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ABSTRACT TEXT

Organic light-emitting diodes (OLEDs) are widely viewed as the basis for next generation displays and lighting. However, to apply this technology widely and for it to reach its full potential, improvements in the emission efficiency and device lifetimes are vital. So far the development of new emitters in OLEDs is mainly empirical in nature that results in slow progresses in the finding of highly efficient emitters. Therefore being able to predict the emission efficiency prior to the synthesis and measurement of properties is of crucial importance for the discovery of new highly efficient emitters. Our recent work[1] has shown that it is possible to predict the emission efficiency through the calculation of the radiative rate[2] and non-radiative rate[1] using state-of-the-art computational strategies. Specifically, we find that the main non-radiative process of a series of iridium(III) complexes is the elongation or even breaking of a metal-ligand bond, and the non-radiative rate can be predicted from the energy barrier to this non-emissive state. In this talk, I will present our recent advances in predicting the emission efficiency of a new series of deep blue light-emitting complexes that allows us further proposing new highly efficient deep blue emitters for OLEDs.

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Prediction for anisotropic carrier mobility of tilted Dirac cones

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ABSTRACT TEXT

The recent synthesis of three phase of monolayer borophene on Ag (111) substrate has opened the era of two-dimensional (2D) boron sheets. The 8-Pmmn borophene and borophane (fully hydrogenated borophene), which were predicted to have a lower formation energy than the borophene prepared in the experiment, both have tilted Dirac cones, the first in non-graphene-like 2D materials. We propose a general formula for predicting the mobility of tilted Dirac cones by using the Boltzmann transport equation coupled with the improved deformation potential theory (considering both the longitudinal acoustic (LA) and transverse acoustic (TA) phonon modes). Combined with the specific calculation of 8-Pmmn borophene and borophane, it indicates that the effect of the tilt factor on the mobility can't be ignored and has a significant reduction effect. Intriguingly, the predicted intrinsic mobility of 8-Pmmn borophene is anisotropic ($11.7\times10^5 cm^2V^{-1}S^{-1}$ and 23×10^5 $cm^2V^{-1}S^{-1}$ in x and y direction respectively at room temperature) and is even larger than that of the graphene (10^6 $cm^2V^{-1}S^{-1}$). The intrinsic mobility of borophane are calculated to be $2.73\times10^5 cm^2V^{-1}S^{-1}$ and 7.47×10^5 $cm^2V^{-1}S^{-1}$along x and y direction at room temperature, which are comparable to graphene. The movements of the Dirac cones in these two materials under small strains are also discussed

PREPARATION OF NOVEL FILM FORMING POLYMER LATEXES USING COLLOIODAL NANOPARTICLES AS EMULSION STABILISERS

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Polymer latex particles can be prepared in the absence of surfactants through a Pickering-type emulsion polymerisation process. Colloidal silica nanoparticles are used to prepare film forming latexes for application in waterborne exterior paints. Colloidal stability is provided by the nano-sized solid particles that irreversibly adhere to the surface of these latexes, effectively replacing the role of surfactants. Conditions were investigated to understand how the maximum adsorption of nano-particles onto the surface of the latex is achieved such that the resultant latex is completely armoured in nano-silica. The oil-in-water emulsion polymerisation process uses methyl methacrylate (MMA) and butyl acrylate (BA) as co-monomers, along with a water-soluble initiator, in the presence of a solution of colloidal nano-silica, commercially available as a colloidal stabiliser in the form of Ludox-TM 40. The pH of the solution was reduced to pH 4.5 before polymerisation and through either the addition of very small amounts of methacrylic acid (MAA) or vinyltriethoxysilane (GF-56), latexes that are completely armoured in colloidal nano-silica are produced. The latexes were characterised by SEM, Cryo-TEM and AFM imaging techniques. The mechanism behind this adsorption is to be investigated in the future through pendant drop tensiometry and horizontal ATR-FTIR in order to understand the factors that influence this irreversible adsorption.

PREPARING FOR PROFESSIONAL PRACTICE THROUGH AUTHENTIC LEARNING AND ASSESSMENT

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ABSTRACT TEXT

As the higher education system produces ever more graduates and the graduate employment landscape becomes more competitive, we need to ensure that an education in chemistry can prepare graduates to succeed in the work environment. If we are to prepare students for professional practice then the chemistry curriculum and the pedagogy through which it is delivered must change. Employers and graduates themselves are clear that universities are failing to deliver the skills and competencies required (Sarkar *et al*., 2016). To prepare students for professional practice we must model and mimic such practice in learning and assessment tasks. Thus a move towards authentic learning activities coupled with authentic assessment will develop an understanding of the professional practice required of the chemistry graduate. This presentation will introduce a simple tool that can be used to evaluate the authenticity of learning situations and assessment tasks. The tool can be used to support a move to a more authentic curriculum and pedagogy to help meet the needs of our graduates.

Graduate Employability: Views of Recent Science Graduates and Employers**,** M Sarkar, T Overton, C Thompson, G Rayner, *International Journal of Innovation in Science and Mathematics Education,* 2016, **24**, 3, 31-48.

PRESSURISED HOT WATER EXTRACTION: NEW APPROACHES TO NATURAL PRODUCT ISOLATION

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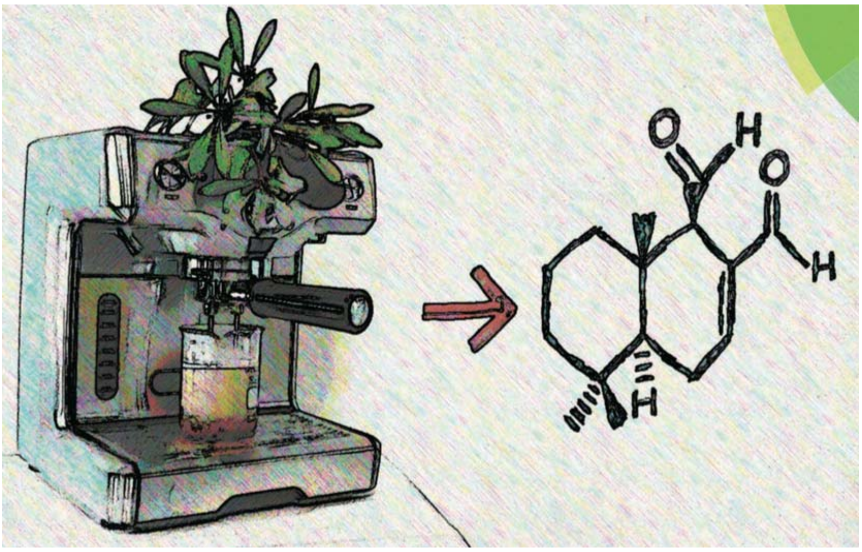
Natural products remain an important source of inspiration for new organic scaffolds for medicinal chemistry. The development of efficient techniques for the isolation of these scaffolds is therefore desirable. This work is concerned with the development of a new method for the extraction of biologically interesting organic scaffolds from plant material. This is achieved using pressurised hot water extraction (PHWE) using a standard household espresso machine. The new method has been compared to traditional methods of isolation, and provides superior results. It is possible to isolate gram scale quantities in a short period of time with relative ease as the crude extracts are relatively clean, simplifying the final isolation. The isolation of natural products and applications to the discovery of biological active molecules will be presented.



PRIMER TUTORIALS TO SUPPORT STUDENT LEARNING IN FIRST YEAR CHEMISTRY

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The large first year chemistry course at the University of South Australia has become more complex in recent years due to changes in prerequisites for entry into our suite of undergraduate degree programs. This has led to the student cohort having a much greater diversity of prior exposure to chemistry than was previously the case. This ranges from year 12 chemistry experience through to never having studied chemistry before. Engaging and supporting such a broad array of students therefore presents a significant challenge. This increasing diversity of students has led to the innovation of “primer tutorials”. These extra tutorials for students with a limited chemistry background are provided at the beginning of each teaching week, and provide an introduction to the “fundamental concepts” of the course material in the week ahead.

This presentation will focus on the implementation of these tutorials, and discuss the evidence collected demonstrating that they have been successful. It is clear from analyzing primer tutorial attendance that the students with a limited chemistry background who attend these tutorials have a much higher rate of success in passing Chemistry 100 compared to those who do not attend. The successful integration of students without a year 12 chemistry background into the Chemistry 100 course (now ~25-30% of the cohort) has not been without its difficulties, but has been able to be achieved without sacrificing course quality or significantly increasing failure rates.

PRINTED LARGE AREA ORGANIC ELECTRONIC DEVICES: MATERIALS, FABRICATION AND CHARACTERISATION

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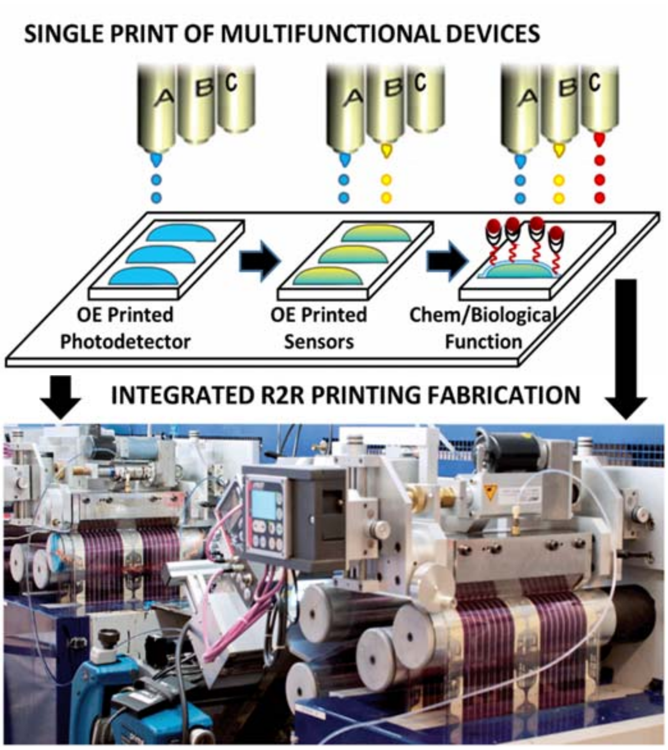
ABSTRACT TEXT The enormous demand for consumer electronics has generated an urgent need for new hybrid electronic materials that can be deposited over large areas using low-cost fabrication techniques. This demand has created intense interest in printed organic electronics, a field which focuses on the use of multifunctional electroactive inks to manufacture electronic circuits and devices on flexible substrates using roll-to-roll (R2R) processing techniques.

Organic electronic (OE) materials have attracted particular interest as ideal candidates for printed electronics applications. The suitability of OE materials for this purpose arises from the ability to modify their chemical, physical and electronic properties and control their film-forming mechanisms through conventional wet chemistry. Beyond the materials challenges themselves, a detailed understanding of the physical chemistry governing the printing and coating techniques that allow the controlled deposition of high-quality OE films are required to address the unique fabrication challenges posed by soft organic materials and large area R2R fabrication.



Here we will report some of our recent advances in the synthesis of electroactive materials and inks on the large scale for roll-to-roll printing of electronic devices. We will describe the materials challenges encountered and the new physical chemistry insights uncovered in transitioning from traditional lab scale fabrication to the R2R printing and coating methods. Finally the subsequent fabrication and characterisation of devices prepared from these materials will be discussed. These include the production, characterisation and installation of 100 m^2 of printed solar cells, fabrication of transistors for saliva-based glucose sensing, activation of organic electronic sensors using light coupled from an optical fibre and the printing of plasmic bridgewires for explosives detonation timing and initiation.

Probing Carbohydrate Structure With Raman Optical Activity (ROA)

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ABSTRACT

Raman optical activity (ROA), which measures a small difference in Raman scattering with right- and left-circularly polarized light from chiral molecules, has proven over the last two decades to be a highly useful probe of solution-phase conformation of proteins and peptides [1]. More recently, the exquisite sensitivity of ROA to stereochemistry has been used to investigate the structure and behaviour of carbohydrates, which are arguably the most important (99% of the planet's biomass is carbohydrate) but least understood class of biopolymers. Despite the undoubted importance of carbohydrates, our knowledge of their structure-function relationships is limited due to the limited applicability of high resolution methods. We have previously shown that ROA has great potential in structural glycobiology [2,3], and here we outline our recent work on the conformational stability of mono- and polysaccharides.

Furthermore, we have pioneered quantum mechanical (QM) modelling of carbohydrate spectra, coupled with molecular dynamics (MD) simulations, to investigate the conformational dynamics of sugars at the atomistic level [3-5]. This combined computational-experimental strategy establishes a powerful and novel approach for structural glycobiology. This presentation will describe the principle steps in this process and discuss key results.

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PROBING MOLECULAR LEVEL THERMAL OXIDATION OF JET FUELS WITH GC×GC-QTOFMS

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ABSTRACT TEXT

Oxidation of aviation fuels affects the safe operation of high performance aircraft. The use of fuels as cooling fluid in fighter jets means that they are exposed to increased heat loads over an extended period of time, which induces autoxidation reactions of the fuel hydrocarbons. The formation of oxidised species generated in these oxidation reactions is implicated in the formation of insoluble deposits in fuel systems, and also the development of undesired fuel properties such as poor water separability. As the use of synthetic and other alternatively-derived fuels increases around the world, it is important to understand the process occurring at a molecular level.

This study reports the use of comprehensive two-dimensional gas chromatography (GC×GC) with accurate mass time-of-flight mass spectrometry (QTOFMS) to study oxidised species in complex aviation fuel matrices. GC×GC-QTOFMS was applied to the analysis of thermally oxidised conventional and alternate jet fuels. GC×GC analysis allowed an enormous range of oxidised species to be isolated and identified, including multiple homologous series of important oxygenates. These advanced separations and detection modes also facilitate the quantitation and correlation of a number of compounds with established methods for quantitatively assessing fuel stability.

PROBING ROAMING DYNAMICS IN H2CO BY PROBING THE H_2 FRAGMENT BY ION IMAGING

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H_2CO is a prototypical system for the study of roaming reaction dynamics. Extensive theoretical and experimental work [1] has gone into establishing and characterizing roaming as a genuine alternate pathway to molecular products. Experimental [2] work to date has focused predominantly on the CO (v = 0, 1) photo-fragments, which gives a complete picture of the product state distributions of the corresponding H_2 co-fragment. Currently there are no data on higher vibrational states of CO and no direct observation of the H_2 photoproducts from this reaction.

In this work we fill this gap using Velocity Map Ion Imaging to measure the KE distributions of state selected H_2 photo-fragments. The results are surprising – the roaming channel, at threshold, produces CO excited up to v = 3, with some degree of vector correlation previously thought not to exist in roaming pathways. Higher vibrational levels of H_2 (v > 5) have generally been associated with the roaming channel. Here, we provide evidence that highly rotationally excited H_2 in v = 6, 7 is also produced via the TS pathway.

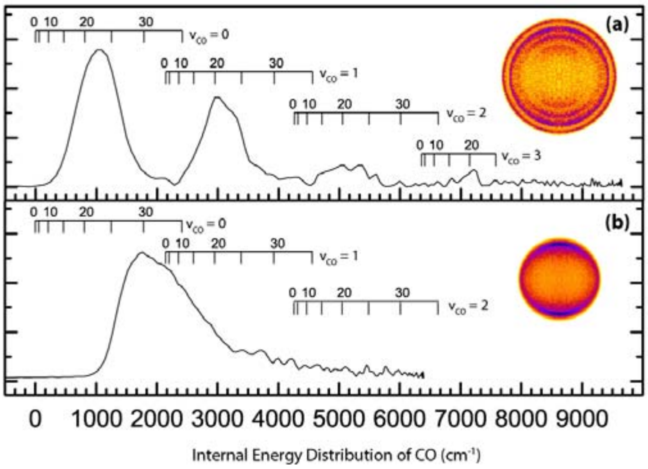

Figure 1: VMI images of H_2 v = 6, (a) J_{H2} = 2 and (b) J_{H2} = 10, following dissociation of H_2CO excited to the $2^1 4^3$ (S_1) state.

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Probing the gas phase structure of ionised lipids

Blanksby, S. J.,[1] Poad, B. L. J., [1] Maccarone, A. T.,[2] Mitchell, T. W., [2] Yu, H.,[2] Bull, J. N.[3] and Bieske E. J.[3]

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ABSTRACT TEXT

The field of lipidomics aspires to identify and quantify all lipids in biological systems to reveal the complex molecular-level dynamics brought about by genetic changes or environmental stressors. Currently, the true scale of this challenge is unknown, with some estimates suggesting that a cellular lipidome could constitute as many as 180,000 structurally distinct compounds. With no genetic roadmap to unequivocally establish which lipids should be present, lipidomics has become a proving ground for the sensitivity and structural selectivity of bioanalytical methods. At the forefront of these technologies has been mass spectrometry, which is capable of detecting hundreds of lipids in extracts from very small amounts of tissues or even just a few cells. Powerful high-resolution mass spectrometers can assign the elemental composition to ionised lipids but are currently limited in their ability to unequivocally assign the molecular structure. Key to surmounting this problem is understanding the structure and reactivity of ionised lipids within the vacuum environment of the mass spectrometer. Such fundamental insights will provide the necessary handles to be exploited for unique lipid identifications in complex mixtures. In this presentation, we outline the use of ion-mobility spectrometry, ion-molecule reactions and molecular dynamics simulations to probe the structure of simple ionised lipids in the gas phase. These investigations reveal critical interactions between the charge and sites of unsaturation within the lipid that define its three-dimensional structure and reactivity. Translation of this knowledge to the elucidation of unknown lipid structures will be demonstrated.

Products of Reactions of Carbonyl Oxides

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ABSTRACT TEXT

The ozonolysis of alkenes forms carbonyl oxides, closed-shell singlet species that are nonetheless relatively reactive. Since the discovery that reactions of α-iodoalkyl radicals with O_2 could produce carbonyl oxide Criegee intermediates in sufficient quantity to directly measure their reaction kinetics, many groups around the world have been investigating these potentially important tropospheric reactants. The initial direct kinetics investigations showed that many reactions of Criegee intermediates are substantially more rapid than had been inferred from more indirect measurements. Knowledge of the products of these reactions is now of increased interest for atmospheric chemistry, and interrogation of products is a key means to analyse the mechanisms of the reactions. The isomer-selective technique of multiplexed synchrotron photoionization mass spectrometry that enabled the first detection of gas-phase Criegee intermediates has now been employed to identify isomeric products of their reactions. I will highlight recent work that has focused on Criegee intermediate isomerization and on products of reactions of Criegee intermediates with species such as NO_2 and organic acids.

Masked Fluorophores: Profluorescent Nitroxides as Reversible Real-time Monitors for Cellular Redox Status

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ABSTRACT

Nitroxides are powerful antioxidants and very efficient free radical scavengers. Significantly, when the nitroxide group is combined with a fluorophore, the usual fluorescence emission is essentially short-circuited. Reaction to the diamagnetic state however, restores the natural fluorescent nature of the conjugated system. This then allows the monitoring of radical reactions by the level of fluorescence emission generated[1] as the nitroxide is converted to the fluorescent (and diamagnetic) product. We have described such nitroxide-fluorophore systems as profluorescent nitroxides (PFNs)[2] and used them to probe the basis of oxidative diseases[3], as sensors for damage in materials[4] and even for monitoring pollution from ultra-fine particles[5]. In living systems the ultimate fate for any nitroxide, is *reduction* to the hydroxylamine[6], as cells use some of their reductive capacity to convert the nitroxide to the non-radical species. This reduction process presents a unique means to determine the overall redox "health" of living systems. Our PFN probes reflect, in real-time and reversibly, the overall oxidative status of cellular systems and respond to any redox changes including the addition of drugs and stresses applied over time.

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PROGRESS TOWARDS HYDROGEN AND AMMONIA FROM RENEWABLES

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ABSTRACT

While the technology of water electrolysis is well established, significant advances in efficiency are required to make the process competitive as an energy storage mechanism. Improvements are needed in catalysts for both the hydrogen evolution and the oxygen evolution reactions. The latter is particularly sluggish and much attention has been devoted to understanding and developing new catalysts and media for this reaction. Ionic liquids have proven to be valuable in this regard.

The energy source for this electrolysis process can be a renewable electricity sources, including “excess” energy in power grids at times of excess supply. As an alternate to this “grid connected” mode, recent work has demonstrated the levels of “Solar-to-Fuel Efficiency” (>22%) that can be achieved with direct connection of the electrolysis cell to the photovoltaic cell.

Where the source of the renewable energy is geographically distant from population centers (“Stranded Renewables”), the issue of hydrogen storage and transportation arises. One solution to this challenge that is being explored is the use of “renewable” hydrogen to generate liquid ammonia, which relatively easily and safely transportable by both pipeline and marine tankers. The capacity for the generation of renewables in the remote areas of Australia is immense, and converted to ammonia could be easily transported for conversion into hydrogen at a relatively local level.

This talk will discuss the underlying electrochemistry challenges of these important renewable energy processes and the role of ionic liquids in some aspects as unique media in which to carry out the process.

Protein structure and dynamics through the lens of solid-state NMR

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Solid-state NMR is a powerful, complementary to other biophysical techniques, approach for studying at atomic resolution structures and dynamics of proteins in various forms from fibrils and membrane proteins to large protein complexes. In this presentation, I discuss several developments in methodology and applications concerning protein structure and dynamics in the solid state with examples illustrating advantages and challenges of the above-mentioned approach.

Protein-mediated controlled radical polymerization

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ABSTRACT TEXT

Recently, the principles of "green" chemistry have attracted the attention of scientists, including those in the field of polymer synthesis. As a subset of this field, the use of biocatalysts (i.e., catalysts derived from biological sources such proteins) for synthesizing well-defined polymers remains an underexplored area of polymer science. In the present work, a synergistic combination of two proteins is demonstrated to mediate a reversible addition-fragmentation chain transfer (RAFT) polymerization via the Fenton reaction in the presence of dissolved oxygen. The mechanism of biocatalyst activation, as well as the optimization of catalyst loading levels is investigated for the synthesis of well-defined linear polymers (**Figure 1**), with a view towards the potential for these materials to be utilized in biologically-relevant applications.

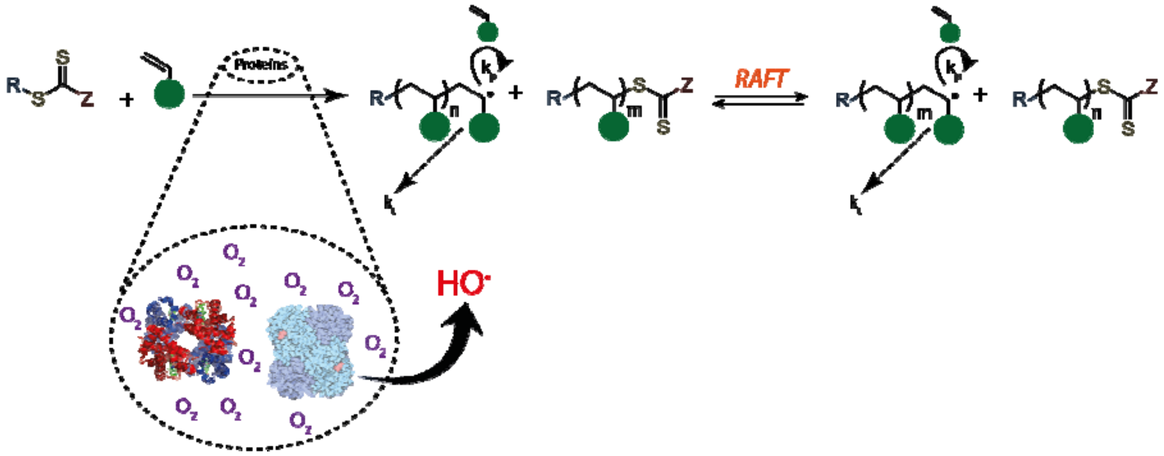

Figure 1. Basic schematic of protein-mediated synthesis of well-controlled polymer.

Protomer-specific photochemistry using tandem ion mobility mass spectrometry

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Protomers are structural isomers of molecules that differ in protonation site. Because protomers are isobaric, they are difficult to distinguish with conventional mass spectrometry. Here, we use tandem ion mobility mass spectrometry coupled with laser spectroscopy to investigate protomer-specific photochemistry in the gas phase. Ion mobility spectrometry is a gas-phase analogue of chromatography or electrophoresis, in which isomers are separated based on their collision cross-sections with an inert buffer gas (~6 torr pressure in this work) as they move under the influence of an electric field.

We show the DCM dye molecule in the gas phase has three protonation sites as well as *cis-trans* isomers relative to a central double bond. The protomers observed in our experiment are assigned by considering ion mobility arrival time distributions as a function of ion source conditions, buffer gas (He, N_2 or CO_2), and theoretical calculations. We show that two of the *trans* protomers produce unique S_1 state photoisomerisation bands, shifted by ~200 nm relative to one another. In contrast, the *cis* protomers are indistinguishable with ion mobility and do not give any discernible photoisomerisation, suggesting that fluorescence and internal conversion pathways are more probable than isomerisation pathways. The protomer-specific photoisomerisation can be explained by considering changes in charge-transfer character of the S_1 state with protonation site. Overall, DCM provides the first clear example of protomer-specific photoisomerisation.

Pyrrolizidine Alkaloids – Natural Toxins from Flowers to Honey

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ABSTRACT TEXT

Pyrrolizidine alkaloids are carcinogenic esters and di-esters of 1,2-unsaturated pyrrolizidine bases which are found in more than 3% of all flowering plants, particularly *Heliotropium, Crotalaria, Echium* and *Senecio* species. The prolonged intake of these alkaloids in food or feed is known to cause chronic liver toxicity in both livestock and human populations. The dietary intake of products containing these alkaloids (e.g. contaminated grains, teas and medicinal products) is of greatest concern and Food Standards Australia New Zealand (FSANZ) have established a provisional tolerable daily intake for these alkaloids of 1 µg/kg BW/day. Bees are also known to transfer these alkaloids from flowers to honey, and concern has been raised as to the extent of this contamination in Australian honeys. Prior to the introduction of control measures in pastures, the introduced plant species Paterson's Curse (*Echium plantagineum*) had been reported as a source of honey contamination with alkaloids previously detected at concentrations up to 2000 µg/kg in honeys from southern regions of Australia. In the present study more than 150 samples of both blended and mono-floral honey were sourced from markets and supermarkets in Queensland and analysed by LCMSMS for some 13 common pyrrolizidine alkaloids, including those present in *Echium plantagineum.* Alkaloids of *Echium plantagineum* and *Senecio* species were detected in some honeys, but the more predominant pyrrolizidine alkaloid contamination (at up to 4500 µg/kg) had a composition related to Blue Heliotrope (*Heliotropium amplexicaule*), a common plant in lawns and pastures in temperate and sub-tropical regions of eastern Australia.

QUANTITATIVE PPCP ANALYSIS IN INVERTEBRATES USING LC HIGH-RESOLUTION MASS SPECTROMETRY

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Liquid chromatography and mass spectrometry have been considered as two of the most important tools to identify and quantify pharmaceuticals and personal care products (PPCPs) in different environmental matrices. Hence, these techniques have been increasingly applied for environmental assessment in recent years. Mass accuracy, resolution, scan speed and the capability of MS/MS are all key factors which affect the quality of analysis, especially at trace levels. In this study, a comparison between two advanced systems of LC/MS was conducted. The two systems consisted of an ultra-high-performance liquid chromatography hyphenated with quadrupole Orbitrap mass spectrometry (UHPLC–QOrbitrap MS), and a HPLC hyphenated with accurate-mass quadrupole time-of-flight MS (HPLC–QTOFMS). Freshwater invertebrate samples were extracted using QuEChERS methods and analysed by both systems under equivalent chromatographic conditions. Although both systems showed high sensitivity for analysis of the samples at very low concentrations, the Q Exactive Plus system was more sensitive as in most cases full scan was sufficient to quantify the analytes at very low concentrations. This system also provided higher quality fragmentation data which can be useful to confirm compound identities in environmental samples, which is important for untargeted analysis. The lowest concentration that can be detected in full scan mode was 0.01 $ng.g^{-1}$ for the Q Exactive Plus system whereas it was 0.1 $ng.g^{-1}$ for the Q-TOF system, for analytes that are well ionised. Both systems showed excellent mass accuracy of below 5 ppm for most of the analytes although the Orbitrap instrument provided more accurate results for some PPCPs.

How Quantitative Structure-Activity Relationship (QSAR) approaches are used in Australian Chemicals Regulation

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ABSTRACT

The international emphasis on reduction and replacement of testing in animals has increased the utilisation of alternative approaches, such as (Quantitative) Structure-Activity Relationships (SAR/QSAR), for evaluating potential (eco)toxicity of chemicals. At the same time, national and international regulatory programs seek to evaluate the hazards and risks from chemicals in use for which significant paucity of measured data has been identified.

The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is a statutory body within the Department of Health responsible for aiding in the protection of the Australian public and environment by assessing the risks posed by industrial chemicals, as well as providing information to promote their safe use. NICNAS is addressing the unknown human health and environmental impacts of unassessed industrial chemicals on the Australian Inventory of Chemical Substances (AICS). NICNAS established the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework to accelerate the assessment of risks posed to human health and the environment by previously unassessed chemicals listed on the Australian Inventory of Chemical Substances (AICS).

In the current IMAP assessments, (Q)SAR methods are used in the weight of evidence considerations where available experimental data are lacking or are either conflicting or of limited reliability. These methods are also useful in providing a suggestion of the mode of action or mechanistic interpretation of an (eco)toxicity endpoint of the chemicals being assessed.

An overview of how NICNAS utilised (Q)SAR approaches in the prioritisation and assessment of industrial chemicals will be presented.

Quantum molecular dynamics for multidimensional systems by BEL MCG

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Quantum molecular dynamics simulations of chemical reactions are needed to fully understand the dynamical processes of molecules. Accurate wave-packet propagation is an attractive means of attaining accurate quantum molecular dynamics simulations. The variational multi-configuration Gaussian (vMCG) method uses localized Gaussian functions as a basis set to perform wave packet calculations. vMCG has shown some success in carrying out wave-packet propagation. In vMCG time evolution, the equations of motion for the expansion coefficients and the parameters of Gaussian basis functions have to be solved. vMCG, however, requires a large number of Gaussian basis sets for tunnelling cases, which are often the most important aspect of chemical reaction simulations, and becomes numerically stagnant. The computational cost for solving the equations of motion becomes prohibitive.

Here, the new method what we call the basis expansion leaping multi-configuration Gaussian (BEL MCG) method has been developed. In the BEL MCG, the wave-packet propagation is performed for short times without changing the basis of Gaussian functions and then re-expression of the propagated wave function is carried out to yield a new basis set adapted to the time-evolved wave function. The BEL MCG can be used the propagation of the multidimensional systems because the rapid increase in the number of the basis functions for tunnelling scenario can be inhibited and the difficult propagation of basis function parameters is avoided. This talk will describe recent developments in the formulation and application of BEL MCG to a several representative reaction profiles and setups.

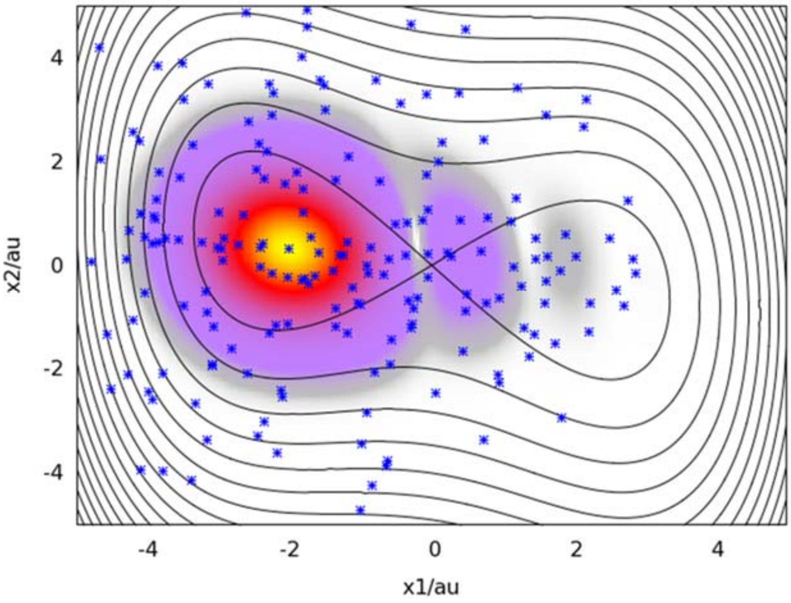

Fig.1 A tunnelling case

RADIOCHEMICAL TECHNIQUES FOR RADIOCHRONOMETRY IN NUCLEAR FORENSICS

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ABSTRACT

Uranium series disequilibria measurements have been used for radiometric dating for many decades, mainly for elucidating geological and environmental processes. Recently, such measurements have been applied to the dating of nuclear materials for nuclear forensic applications. In nuclear forensics, one of the key ‘signatures’ used to characterise an unknown nuclear material is the material’s age i.e., the time elapsed since the material was last chemically processed. The ^{230}Th/^{234}U isotopic pair is the most widely employed chronometric system in nuclear forensic examinations, but using two separate parent/daughter pairs to date unknown nuclear material provides increased confidence in the material’s analytically measured “model” age. For this reason, ANSTO has developed the capability to measure protactinium (^{231}Pa, half-life = 32,760 years) by mass spectrometry to enable application of the ^{231}Pa/^{235}U chronometer to uranium bearing samples. Measurement of ^{231}Pa required the development of a method to produce the spike isotope ^{233}Pa by neutron irradiation of Th followed by separation of the Pa from Th and U. This presentation will give an overview of nuclear forensics with reference to several case studies undertaken by the Nuclear Forensics group at ANSTO. The radiochemical procedures developed at ANSTO for dating uranium materials will be presented.

RAFT Polymerisation of Acrylamide by Photolysis of Chain Transfer Agents

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Use of direct photolysis on chain transfer agents (CTAs) to initiate free radical polymerisation has received increasing interest in recent years. In this ‘iniferter’ process, the CTA acts as an initiator while also facilitating controlled polymerisation through reversible termination and degenerative chain transfer (the RAFT process). Photolysis of the CTA can be achieved through γ-radiation, UV irradiation and visible light irradiation.

We have examined the aqueous polymerisation of acrylamide to 10 kDa via direct photolysis of a symmetrical trithiocarbonate CTA. Samples were irradiated at different wavelengths (λ_{max} = 402nm, 451nm) and different intensities in order to better understand the effect of these parameters on polymerisation rate and control. Conversions of >85% were achieved in 20 minutes to 12 hours depending on the wavelength and intensity. Interestingly, polymerisation control was found to be near identical across all conditions with linear and overlapping M_n v conversion plots and similar dispersities (Đ= 1.13 – 1.19).

In addition to the key results of these experiments, a new insight for the characterisation of RAFT polymers by aqueous GPC is also reported. Specifically, the broadening of molecular weight distribution due to dilute sodium azide (often used as a biocide) in the GPC solvent. This phenomenon is demonstrated for a range of polymers prepared under RAFT conditions.

RAFT: a platform technology – antibody-polymer-drug conjugates for biomedical applications

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We have developed a platform drug-delivery technology based on the versatility of the Reversible Addition-Fragmentation chain Transfer (RAFT) process to help deliver polymer-based materials for biomedical applications. The approach is based on developing RAFT technology to address key clinical and technical challenges for the use of polymeric materials in therapeutic delivery systems. We report therapeutic antibody-polymer-drug conjugates, where the polymer acts as a carrier for both a small molecule cytotoxic drug as well as a therapeutic protein, such as an antibody. In order to understand the influence of polymer structure, composition and size on biological performance, we report the results of two, first in class, ADME studies. These studies assess the pharmacokinetics of a range of homo-polymer and co-polymer antibody-fragment conjugates, in animal models (seven RAFT polymers and one control). All of the antibody fragment-polymer conjugates investigated had increased elimination phase half-lives over the PEG control, and although differences were observed within the circulating half-life between the conjugates (arising from the different polymer compositions), the excretion volume is fairly consistent. This result confirms that this range of RAFT polymers are a suitable platform for delivery of proteins and targeted delivery of small molecule drugs. We have conjugated an ADME optimised, complex, high molecular weight, terpolymer containing a number of cytotoxic drugs, attached *via* cleavable linkers, to antibody fragments and the results of a drug-loaded polymer-antibody fragment conjugate (***Figure 1***) *in vivo* efficacy study will be reported.

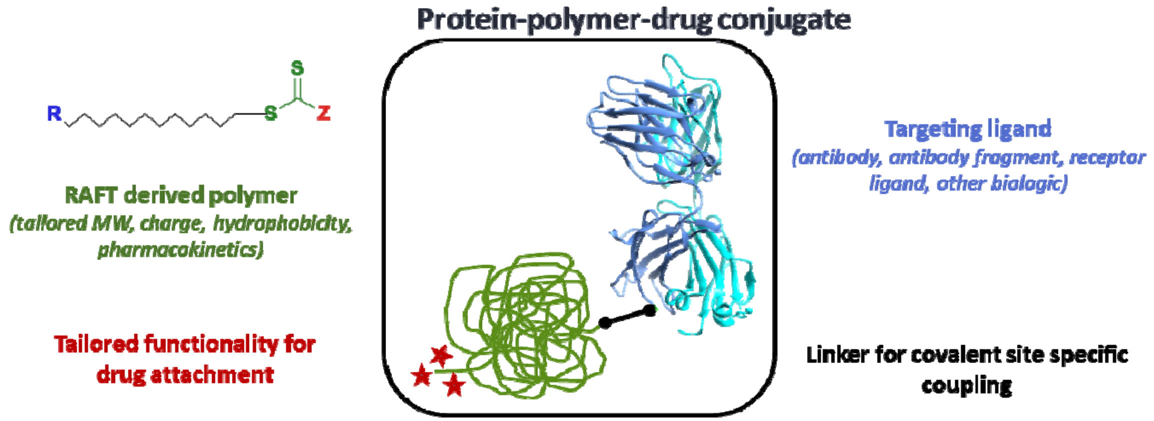

Figure 1: *Protein-polymer-drug conjugates for targeted delivery of cytotoxic drugs*

Rasch analysis of three first year approaches to benchmark Chemistry

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Rasch Analysis, a statistical and probabilistic analysis tool, is being used to examine chemistry exams across subjects and years; the analysis transforms the raw performance of students and exam questions separately - representing “ability” and “difficulty” respectively - into a common scale of measurement called “logit”. It therefore allows the academic to compare the performance of students versus that of the questions using a single understanding of “performance”. The Rasch approach differs strongly from other approaches - as opposed to other statistical approaches Rasch analysis is suitable to measure a single “construct” or constructs that are likely to be correlated. Unlike its counterparts, once validated, this approach is no longer sensitive to cohort size. As to date there have been few applications of Rasch analysis to the examination of university chemistry assessments. This talk will report on how this method has been used to validate exams, examine the coverage/difficulty across and between four different first year chemistry classes, and examine student's performance from a demographic perspective such as course and gender. These results and insights serve as the first step in bridging to work with exams from other Australian universities to benchmark exams, exam questions, subjects (and perhaps student abilities) between universities.

REDOX-NEUTRAL SYNTHESIS OF ISOQUINOLINES VIA PHOTOREDOX CARBOARYLATION OF ACTIVATED ALKENES

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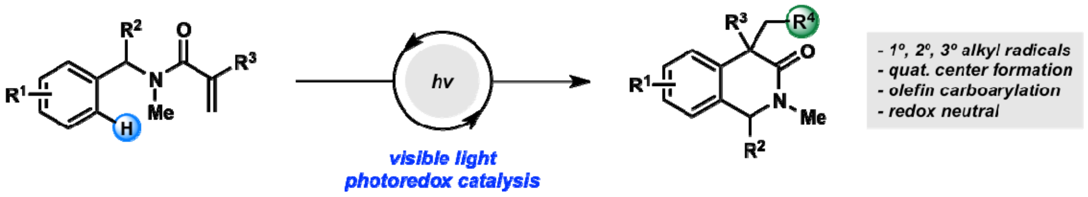
Photoredox catalysis has recently engendered a revival in radical-based methods in synthetic organic chemistry.[7,8] This approach relies on excitation of a metal complex or organic dye with visible light to initiate single electron transfer events at room temperature. Formation of an excited species that can function as both a strong oxidant and a strong reductant enables access to redox neutral transformations that are not possible under traditional redox manifolds. We are interested in exploiting photoredox catalysis to provide rapid and simple entry to a diversity of medicinally relevant heterocyclic scaffolds.

This presentation will detail our work in developing a redox neutral carboarylation reaction that furnishes novel isoquinolines in good yields with broad substrate scope. The reaction is triggered by the formation of alkyl radicals through decarboxylation of an activate ester precursor. Primary, secondary and tertiary alkyl radical species all effectively generate the cyclized products with concomitant formation of a new quaternary carbon center. Ongoing investigations are focused on exploring the applicability of this chemistry to other heterocyclic scaffolds as well as providing a deeper understanding of the reaction mechanism.



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Reduced Graphene Oxides based Label-free Electrochemical Immunosensor for detecting TNF-α

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ABSTRACT TEXT

Cytokines secreted from cells play critical roles in tissue repair, cancer development and progression. Unfortunately, probing what cells "see", and what they secrete as they respond to the surrounding signals is still a major challenge. The ultra-low concentration of cytokine (in the pM range), and extremely dynamic, transient cytokine secretion process make cytokine quantification even difficult. Herein we developed a label-free electrochemical immunosensor based on AuNPs loaded reduced graphene oxides nanocomposites (RGO-ph-AuNPs) for detection of cytokine TNF-α. Uniquely five functional components were introduced in this design: 1) RGO-ph-AuNPs to increase the sensitivity; 2) zwitterion molecules to resist non-specific protein adsorption; 3) monoclonal antibody to increase the specificity; 4) ferrocene labeled graphene oxides (GO) to amplify the signal; 5) aryldiazonium salt chemistry to enhance the stability. Specifically homemade RGO-ph-AuNPs were covalently modified to the gold electrode followed by the attachment of antifouling molecules and TNF-α monoclonal antibodies to form the capture surface. The anti-TNF-α detection antibody was modified to GO tailoring with ferrocene to form the GO based signal probe. Then a sandwich assay was formed on gold surfaces for the quantitative detection of TNF-α by the modulation of ferrocene electrochemical signal. The prepared electrochemical immunosensor were successfully used for the detection of TNF-α over the range of 0.1-150 pg mL^{-1} with the lowest detection limit of 0.1 pg mL^{-1}. The immunosensor provided high selectivity and stability, and was capable to detect TNF-α secreted by live BV-2 cells with superior performance to the commercial cytokine ELISA kit.

Re-inventing Immunodiffusion Assays for ASSURED Diagnostics

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There is a pressing need to develop bioanalytical tools that can be used to diagnose diseases. These tools should have the capacity to be used without reliance on laboratory infrastructure and facilities. Immunodiffusion is an inexpensive, simple and one-step technique that allows length-based measurement of antigen levels in samples via the formation of antigen-antibody complexes known as ‘precipitin rings’ in hydrogels. Due to the alignment with the ASSURED criteria (Affordable, Sensitive, Specific, User-friendly, Rapid, Equipment-free, broadly Deliverable), it serves as an ideal candidate for development as a point of care diagnostic device. However, current versions of this assay performed in agarose gels are severely diffusion limited, leading to poor analytical sensitivity and long assay times (up to 24 hrs).

The assay was applied for the first time to the malarial antigen HRP2 and antisera obtained from immunized rabbits. This required determination of an optimum working range of antigen and antisera concentrations. Agarose was used as the material substrate, and the effect of type and concentration of agarose on ring formation was evaluated. Cryo-Scanning Electron Microscopy (cryo-SEM) was employed to observe the porous network structures of gels and determine the pore size distribution. A change in the concentration of agarose leads to a change in the pore size of the gel, leading to increased precipitation ring size, reducing analysis time. The latest results on the formation of immunodiffusion patterns as a function of material properties are presented. (Figure 1)

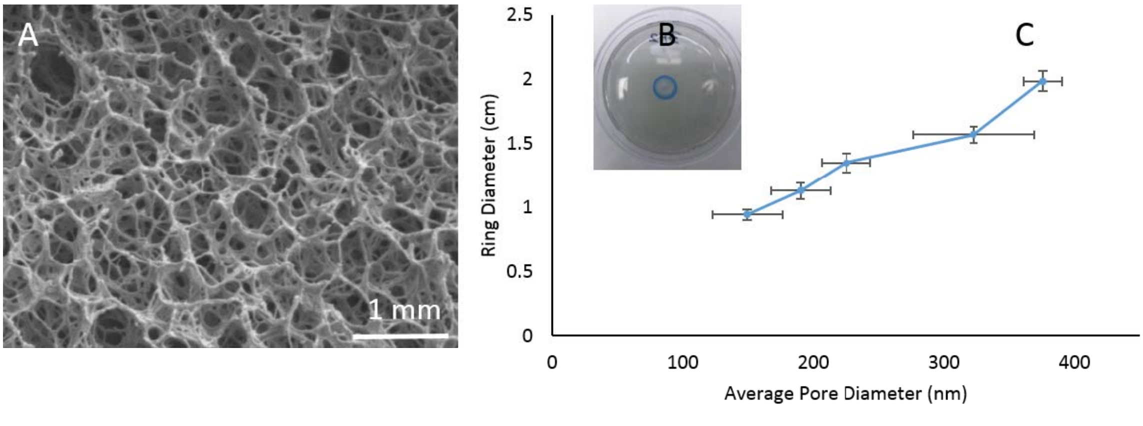

Figure 1: A: Cryo-SEM image depicting the pore structure of a 1% agarose gel. B: A typical gel-based immunodiffusion assay with a precipitin ring. C: Relationship between precipitin ring size and the pore size of agarose used for the assay.

Reliably Determining the Glutathione Redox Ratio in Whole Blood

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Oxidative stress is a cellular condition implicated in numerous diseases including dementia, schizophrenia and Huntington's disease. In the presence of reactive oxygen species, the endogenous antioxidant glutathione (GSH) is converted to its oxidised form, glutathione disulfide (GSSG). This redox couple is extremely valuable in monitoring disease progression and/or drug efficacy, as a change in the ratio of GSH/GSSG is one of the first indications of oxidative stress in the body.

Due to the importance of these biomarkers, a range of analytical methodologies for their determination have been developed. However, it is extremely difficult to ensure that an accurate representation of this ratio is obtained, as GSH can be rapidly converted to GSSG *via* auto-oxidation after sample collection. This is a particular issue in the context of clinical trials, where samples often need to be stored for long periods before bulk analysis is undertaken. Giustarini *et al.* have published extensively describing sample pre-treatment protocols which maintain sample integrity for several months - however this is to the detriment of detection simplicity, as complex derivatisations and multiple assays are then needed to measure both target compounds.

We present here a method which preserves sample stability whilst also allowing for a simple detection strategy which can determine both thiols and disulfides, in whole blood, within a single analytical run. We accomplish this using HPLC combined with multiple detection techniques to develop a rapid and cost effective protocol which requires minimal sample handling – making it well suited to a clinical trial setting.

Researching The Impact Of Large Scale Laboratory Activity Transformations.

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Transforming laboratory learning is a program through which a large number of undergraduate chemistry laboratory activities at Monash University are being redesigned (17 overall units across all year levels). The aim is to increase the amount of inquiry-based learning, as well as to increase the industrial context of the laboratory activities.

The effect of these new laboratory activities are being measured by a) a modified literature sourced survey (Russel, 2008), b) student focus groups run at the end of semester and c) recorded interviews with teaching associates (demonstrators).

The original survey was modified to focus the questions on individual laboratory activities. Three open questions were also added which focused on recognised skill development, potential improvements to the activity and student enjoyment. Furthermore, five new Likert questions focused around student engagement and their perceived degree of control, were inserted into the survey.

Focus groups were run in groups of 2-6 students and questions focused on perceived skill development and enjoyment/engagement. One-to-one recorded interviews with teaching associates focused on their observations around the success of the new activities in terms of skill development and student learning.

The results of four new laboratory activities will be discussed in terms of their success within the aims of the program, as per the survey results and focus group discussions. The evolution of the literature sourced survey will also be fully described and explained. The four laboratory activities varied from industrially focused student controlled exercises through to the simple use of non-traditional methodologies (i.e. not stepwise).

Reshaping the solar spectrum to capture the sun's power

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ABSTRACT TEXT

Photovoltaic (PV) cells show significant promise as a renewable energy resource capable of meeting the world's large and growing energy needs. Increasing device efficiency is central to achieving an economically viable option for widespread applications. Current PV technologies are only able to utilise a portion of the solar spectrum with photon energies above the bandgap. Sub-bandgap losses can be reduced by converting the transmitted light to higher energy, and feeding this back into the solar cell to contribute to current generation.[1] We approach this problem by reshaping the solar spectrum through triplet-triplet annihilation upconversion (TTA-UC); combining two low energy photons to generate a single high energy photon.

This work presents an overview of how we study photon upconversion,[2] including setting a new record for photon upconversion efficiency. Rubrene is an efficient emitter, with upconversion enhancements to current densities exceeding 10^{-3} mAcm^{-2} under one sun excitation,[3] but diffuses slowly which limits its efficiency. In order to increase the device enhancement from upconversion we require a significantly more effective emitter than rubrene. In this work, we used a novel perylene monoimide (PMI) emitter which, when paired with our record setting porphyrin sensitizer, generates >12% TTA-UC efficiency under broadband, one-sun excitation. Further, at just 0.1 suns the efficiency is >4%, six-times that of rubrene. This significant improvement brings us a step closer to realising efficient photochemical upconversion for photovoltaics under low-intensity (sub)-solar conditions.

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SEEKING THE HOLY GRAIL: PREDICTION OF RETENTION TIMES IN LIQUID CHROMATOGRAPHY BASED ON CHEMICAL STRUCTURES OF ANALYTES

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ABSTRACT TEXT

This presentation will report on a large-scale academic-industry collaborative study on the prediction of analyte retention times based solely on chemical structures. The goal of this study is facilitate rapid selection of the optimal chromatographic mode and separation conditions. This study uses Quantitative Structure-Retention Relationships (QSRR) whereby molecular modelling is utilised to generate molecular descriptors of analytes based on their chemical structures. From the large number of descriptors generated, the most relevant descriptors are then determined and a mathematical relationship for an individual unknown analyte is generated which relates the selected descriptors and measured retention times for a test set of analytes. Finally, this relationship can then be used to predict the retention time for the unknown analyte, again based only on its chemical structure.

The above approach has been applied to the prediction of retention times in reversed-phase liquid chromatography (RPLC), hydrophilic interaction liquid chromatography (HILIC), and ion chromatography (IC). In each case, good correlation has been achieved between predicted and observed retention times.

In this talk, a number of key features and questions relating to the QSRR process will be discussed, including the optimal number of descriptors required to provide reliable predictions, the size and nature of the database needed, the range of chromatographic conditions required when measuring retention data, the required accuracy of prediction, and the nature of the analytes used (especially their structural similarity to analytes used to develop the QSRR model). Typical results obtained for RPLC, HILIC and IC will be presented.

Reversible Stereoselective Folding/Unfolding via Interplay of Photoisomerism and Hydrogen Bonding

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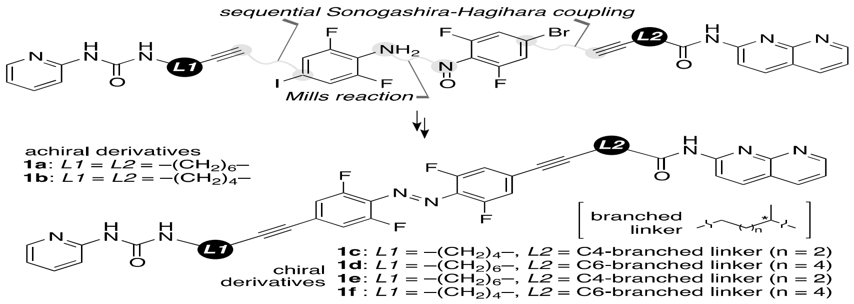
Foldamers represent oligomers and polymers that adopt ordered and compact conformations in solution, mimicking the dynamics of biomacromolecules. Extensive efforts have been devoted to this emerging area to develop dynamic molecules, which seek to close the gap between conventional non-ordered molecules and the exquisite molecular ensembles found in biological systems. Since the folding is often driven by collective non-covalent interactions, foldamers are well suited for the development of dynamic molecules responsive to external stimuli, such as via light irradiation. Merging the concepts of photoisomerization and intramolecular hydrogen bonding present a novel, dynamic method of achieving distinct folded structures.



To achieve this goal a concise synthesis of the above structures was established, which contain a central photoreceptive azobenzene flanked by complementary hydrogen bonding units. Upon stimulation by visible light at >510 nm, isomerization of the central azobenzene unit to the *cis* isomer results in the assembly of a well-defined 3-dimentional folded globular structure held in place by intramolecular hydrogen bonding. Irradiation at 410 nm reverses the process by reverting the azobenzene to the *trans* isomer, resulting in unfolding of the compounds.

The direction of folding - and therefore helicity - of the resultant folded compounds could be controlled by equipping a minute stereogenic element to the backbone at a specific location. This effect was found to be strongly dependent on the overall length of the compounds, with almost quantitative selectivity observed with the shortest compound.

Rhenium(I) and Technetium(I) N-Heterocyclic Carbene Complexes That Bind To Amyloid

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Radiopharmaceutical imaging agents are routinely used for the rapid and non-invasive assessment of organ function and disease diagnosis. We are interested in the use of N-heterocyclic carbene (NHCs) ligands for the development of radiopharmaceutical imaging agents based on metallic radioisotopes and for the first time an NHC ligand has been radiolabelled with the medically important radioisotope Tc-99m.[1,2] We are currently exploring the potential application of NHC ligands for the development of imaging agents for the early diagnosis of Alzheimer's disease. To this end a series of $[Re(I)L(CO)_3]^+$ analogues if Tc-99m imaging agents (where L is a bifunctional bis(NHC)-amine ligand) conjugated to benzothiazole- or stilbene-based amyloid binding groups have been prepared (e.g. Figure 1, a). The Re(I) complexes coupled to the stilbene group bound amyloid-β peptide fibrils and to amyloid plaques in human frontal cortex brain tissue from subjects with Alzheimer's disease (Figure 1, b).[3]

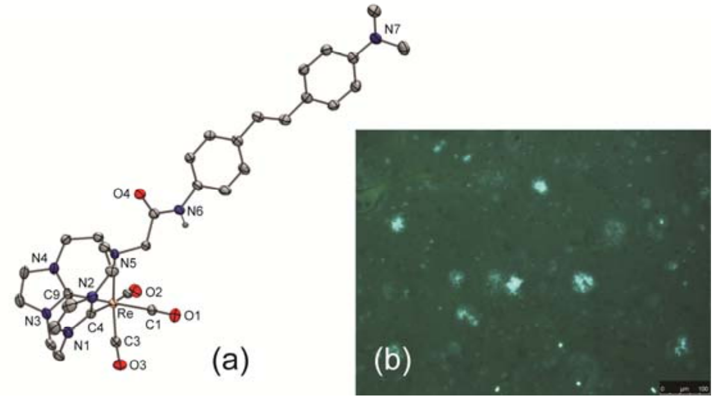

Figure 1. (a) [Re(I)(CO)3]+ complex and (b) AD affected frontal cortex brain tissue stained with Re(I) complex.

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Biological applications which utilise enzymes, or other proteins, require the tertiary structure of the protein to be retained. However, many proteins readily undergo aggregation or denaturation when outside their native environment, and/or over longer timescales. The stability of proteins in solvents other than water is usually considered unappealing due to an assumption that the protein will be insoluble or denatured. However, a few solvents, such as glycerol and dilute alcohols have been shown to have protein stabilising properties.

Previously we have developed extensive structure-property relationships between the chemical structures and mesostructures of non-aqueous solvents and the solvophobic effect experienced by amphiphiles for molecular solvents [1] and protic ionic liquids (PILs) [2]. Here we have extended this to develop a greater understanding of what solvent features are important for protein stability. We have utilised a series of 19 small polar non-aqueous molecular solvents and 4 PILs, with hen egg white lysozyme used for this initial work. Solutions were prepared of the solvents combined with water, and with added precursor acid or base for the PILs, to explore a broad range of pH from 0 to 11.2 and ionicity from 0 to 11 M. These solvent systems enabled us to explore the effect of pH, solvent concentration (ionicity), solvent cohesive energy density and polarity towards protein stability [3]. The secondary and tertiary structure as well as the activity of the lysozyme was determined. This work has the potential to lead to the development of tailored solvent systems to optimise protein stability.

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Room-temperature ESR spectroscopy of an efficient intramolecular singlet fission compound

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ABSTRACT

Next-generation hybrid photovoltaics have emerged as a promising source of renewable energy due to their potential for overcoming the Shockley-Quesser limit. (Tayebjee 2015) In particular, the singlet fission (SF) process (in which a single photoexcited singlet state can be converted to two lower energy triplet states) can result in a significant enhancement of the EQE. (Dexter 1979) Under ideal conditions, the overall singlet triplet-triplet pair state, ^{1}(TT), should decouple into free triplets (T+T), which have a significantly longer lifetime than ^{1}(TT) and are therefore more likely to generate free carriers.

The fundamental dynamics behind the transition of a photoexcited singlet into two triplets with (anti)-correlated spins is not well understood. Electron spin resonance (ESR) spectroscopy is uniquely suited to identifying intermediate states which can limit the efficiency of SF processes. A recent study has found that in dimers of pentacene derivatives, an intermediate quintet state, ^{5}(TT), forms several nanoseconds after photoexcitation, and there exists an energetic barrier to free-triplet generation (T+T). (Tayebjee 2017)

In this work, we will present a systematic study of the spin properties and dynamics of multiexciton states in an efficient intramolecular singlet fission compound (iSF) using a combination of ESR and optical spectroscopy. Additionally, we will demonstrate the effect of spin thermalization on the SF process.

Rural Human Sources of Heavy Metal Concentrations in Fluvial Sediments

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Sources of serious health scares involving the supply of drinking water to cities and towns in Australia focus attention on the environmental status of river catchments. This base-line study reports on the Coxs River that skirts around the Blue Mountains in NSW and is a major catchment of Lake Burragorang for Sydney's water supply. This catchment comprises mainly forests and grazing land but it support a moderate sized city, power stations and coal mines. The heavy metal content of stream-bed sediments characterises environmental flow impact in this rural catchment and sources of contamination. Sediments in a creek flowing through a rural city, Lithgow (population 21,000) were markedly enriched in Cr, Pb and Zn (3x, 18x and 52x, respectively) over background, probably due to a long history of metal-based industry. The highest Cu, Pb and Zn concentrations (204, 332 and 2460 µg/g dry weight, respectively) in fluvial sediments in the town were associated with discharges from a sewage treatment plant. Coal-fired power stations in the catchment contributed Cu and Ni concentrations (maximum concentrations 562 and 157µ g/g, respectively) to ambient fluvial sediments from cooling towers and coal storage areas. The highest Co and Cr concentrations (113 and 490 µg/g) in fluvial sediments of the catchment were associated with coal-mining activities. Selective extraction indicated that about 50% of the anthropogenic fraction might be bioavailable, whereas sequential extraction procedures suggested that <25% was associated with the easily exchangeable/adsorbed phase. Two dams that restrict the migration of heavy metals down the Coxs River and sediment discharges into Lake Burragorang were low in metals. A new study would provide significant data about longevity of levels and impact of changes in the area.

Scaffolding the development of problem-solving skills in chemistry education

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Teaching problem solving and developing problem-solving skills are at the heart of chemistry education. More specifically, the cornerstone questions are: *why do some students struggle with solving problems?* and *how can we help these students develop problem-solving skills?*

Problem solving is a multifaceted activity, influenced by a variety of cognitive, motivational, and behavioural factors. Cognitive factors include content knowledge, understanding of concepts, and process skills. In this study, we focused on approaches for developing students’ problem-solving process skills. Specifically, we have designed, implemented, and evaluated a problem-solving workflow – “Goldilocks Help”. This workflow builds on work done in the field of problem solving in chemistry and provides specific scaffolding for students who experience procedural difficulties during problem solving: dead ends (not being able to troubleshoot) and false starts (not knowing how to initiate the problem-solving process). The Goldilocks Help workflow has been designed to scaffold a systematic problem-solving process with a designation of explicit phases of problem solving, introduce students to the types of questions/prompts that should guide them through the process, encourage explicit reasoning necessary for successful conceptual problem solving, and promote the development of metacognitive self-regulation skills. The tool has been implemented and evaluated over a two-year period and modified based on student and instructor feedback. The evaluation results demonstrated the shift in students’ beliefs in their capacities to use the strategies required to achieve successful problem solving and showed their capacity to employ such strategies.

Screening methods for the radiological assessment of drinking water

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Screening methods are used in the assessment of drinking water supplies as they provide a cheap and rapid measurement of the gross alpha and gross beta activity concentration. The results are then used to determine the need for radionuclide specific analysis. While the preparation of samples for the measurement of gross alpha and gross beta can be considered relatively straight forward there are a large number of factors that may influence the accuracy of the result. World-wide inter-laboratory comparisons have shown wide variability in the results of screening measurements, showing a need for careful consideration of the methodology used.

The Radioanalytical Services Laboratory at ARPANSA has recently established a method for the measurement of gross alpha and gross beta by liquid scintillation counting (LSC). The method enables the laboratory to improve processing time for samples and with the use of scintillation detectors provides spectral information not available in the gas flow proportional counting techniques.

Calibration parameters were established for the LSC screening method as performed by the Radioanalytical Services Laboratory at ARPANSA. Validation of the procedure included Plackett-Burman experimental design to identify variables that may influence the result. These parameters can then be controlled more stringently when conducting the analysis in order to improve the accuracy of the determination.

Seabirds, POPs and plastic

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Concentrations of persistent organic pollutants (POPs) are often high in seabirds due to their position as apex predators. However, monitoring is a challenge due to uncertainty regarding the most reliable and/or non-destructive sampling methods. We investigated the relationship between internal POP body burden and plastic contamination in flesh-footed shearwaters *Ardenna carneipes* and wedge-tailed shearwaters *Ardenna pacifica* from Lord Howe Island. Analysis of liver, kidney, muscle, blood, and feather samples was carried out using selective pressurised liquid extraction (S-PLE) and gas chromatography coupled to triple quadrupole mass spectrometry (GC-QqQ-MS/MS). Results have provided the first baseline data for POPs contamination within Australian species, including polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), as well as the first quantification of novel flame retardants (NBFRs) contamination in seabird species from the Southern Hemisphere. Higher PCB contamination was found in comparison to other contaminants, which is consistent with studies conducted worldwide on species of the same family (Procellariidae). Contaminants appear to preferentially accumulate in the lipid-rich tissues of the liver, while low concentrations found in feathers indicate they may not be the most appropriate non-destructive biomonitoring tools for organic pollutants. POPs levels found within these species from a so-called 'pristine' environment show pollution from a mixture of persistent chemicals is widespread, relevant and urgent issue requiring further research.

Seasonal and Geographical Effect on the Chemical Signature of Milk

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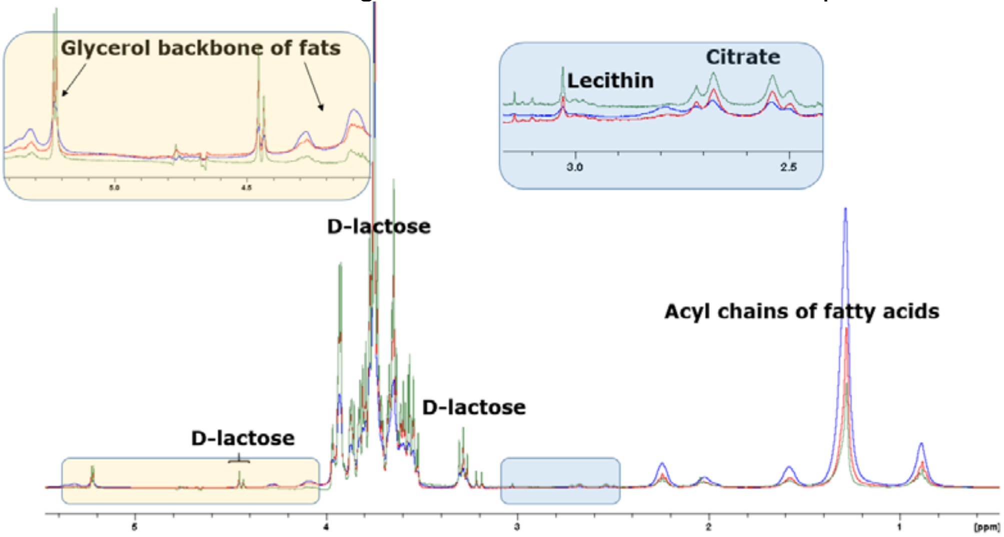
Milk is a primary source of nutrition for mammals in infancy and remains a critical component of the adult diet. As such, milk and dairy production is of great importance on a global scale. New Zealand is the ninth largest producer of dairy products in the world and exports approximately 95% of its dairy production.[1]
Bovine milk is comprised of a complex mix of metabolites which affect the quality of milk. The quantity and composition of these metabolites in milk can be influenced by a number of factors, including bovine species, age, stage of lactation, farming method and seasonal variation.[2,3] Of particular interest to us is the effect of season and sub-region on the metabolome of milk.
Metabolite composition can be comprehensively studied through a number of spectroscopic techniques, including NMR, LC/MS, GC/MS and IR. The results of these spectroscopic measurements can then be analysed through untargeted statistical machine learning methods to identify differences and variation.
We present the results of our study where we explored the chemical signature of raw bovine milk and the affect of sub-region and season variation on this profile.



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Second-generation analogues of the “new” TB drug bedaquiline

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ABSTRACT

Tuberculosis (TB), caused by the bacterium Mycobacterium tuberculosis (M.tb) is again a disease of major concern, due to the rapid increase of both multi-drug resistant TB (MDR; ~480,000 cases in 2015 [3.3% of total new cases], 50% treated successfully) and extremely drug-resistant TB (XDR; ~50,000 cases in 2015, 26% treated successfully). There is therefore a great need for new drugs with novel modes of action and activity in drug-resistant TB.

The drug bedaquiline (Sirturo; Janssen), registered in 2012, inhibits the c subunit of the M.tb ATP synthase and shows promise in drug-resistant TB, but has a number of limitations, including cardiovascular effects (due to its hERG blockade) and phospholipidosis (due to its very high lipophilicity).

Despite this promise, and the limitations observed, there has been relatively little work reported on the development of improved analogues of bedaquiline. We present the results of an extensive structure-activity relationship study of more than 600 analogues of bedaquiline, carried out in collaboration with the Global Alliance for Tuberculosis and Janssen Global (originator of bedaquiline). Separate evaluation of changes to each of the four sidechain units of the drug (A-D), and combination of these to optimize the overall profile, resulted in the selection of six lead compounds. From these, TBAJ-587 was selected in late 2016 as a clinical candidate. TBAJ-587 is currently in advanced evaluation, with the aim of beginning clinical trials in 2018.

SELF-ASSEMBLED LIPID LYOTROPIC LIQUID CRYSTALLINE NANOPARTICLES AS POTENTIAL NANOMEDICINES

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ABSTRACT TEXT

Advances in material science and cancer research have provided great momentum in the development of nanoparticle-based drug delivery systems to revolutionize precision-based cancer treatment and diagnosis. Nanoparticle-based drug delivery systems can offer many advantages over free drugs including: enhanced payloads of hydrophobic drugs, protection of the drugs from premature degradation and interaction with the biological environment, controlled release of the drugs and hence improved pharmacokinetic and distribution profiles, and last but not least targeting mechanisms to specific cells/tissues to reduce the side effect of chemotherapeutic drugs. One class of nanoparticles, the self-assembled lipid lyotropic liquid crystalline nanoparticles (LCNPs), stand out from the crowd offering inherent features of complex three-dimensional nanostructures, high surface area, and extensive porous networks. This presentation will discuss two important aspects in the field of LCNP-based drug delivery systems. First, we will provide an overview on physicochemical properties of LCNPs and their structural flexibilities using lipid additives and polymers. Second, we will present our recent advances on engineering multifunctional LCNPs and their applications in an ovarian cancer xenograft model. This study shows LCNPs were loaded with chemotherapeutic drugs (paclitaxel) or imaging agents and conjugated with epidermal growth factor receptor (EGFR) antibodies as a targeted drug delivery system, inhibiting tumour growth in an ovarian cancer animal model.

Self-Assembly Based Techniques Towards Non-Spherical Polymer Particles

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ABSTRACT:

Polymeric nanoparticles find a wide variety of applications in areas as diverse as material science, health care products and nanomedicine. The traditional focus has been on spherical particles, simply because this geometry is by far the most accessible from a synthesis perspective. Recent progress in the area of radical polymerization in dispersed systems via the so called polymerization-induced self-assembly (PISA)[1,2] approach has opened the door to facile and large scale preparation of nano-objects with more complex non-spherical shapes such as worms, rods, and vesicles. These novel nano-structures typically exhibit very different properties from their spherical analogues. Hollow polymeric nanoparticles, including vesicles, represent another interesting category of nano-objects with wide applications in *e.g.* nanomedicine.

This presentation will be concerned with our recent progress in the general areas outlined above, focusing on the use of self-assembly based approaches for synthesis of polymer particles of a wide range of morphologies. In particular, we have explored ways whereby the particle morphology can be tuned by use of CO_2 as an environmentally friendly and versatile tool to exert influence on heterogeneous polymerization systems. We are also exploring the use of surfactant self-assembly into various structures, including non-spherical structures ranging in size from nano- to micronscale, followed by radical polymerization to permanently “fix” these structures (templating).

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Semi-crystalline Conjugated Polymers for Fullerene and Nonfullerene-based Organic Solar Cells

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Over the past few decades, polymer solar cells (PSCs) have made a significant progress, showing their potential in low-cost, flexible, lightweight, portable and large-area energy-harvesting devices. Although $PC_{61}BM$ and/or $PC_{71}BM$ structures have been exploited successfully in PSC devices, efforts to modify the fullerene structures for further improving the device performance have been unsuccessful due to the inflexibility in molecular design, difficult purification, poor morphological stability, and limited light absorption in the visible region, etc. In recent years, nonfullerene acceptors have emerged as an alternative candidate of n-type materials to overcome the difficulties of fullerene derivatives in tuning optical and electronic properties. The strong and easily adjustable absorption characteristics of nonfullerene acceptors have been considered a strong point compared to fullerene-type structures, showing a photovoltaic efficiency over ~10%. To further optimize the nonfullerene PSCs, controlling the BHJ morphology in the active layer is a critical requirement. Here we discuss the fundamental correlations between molecular structure, blend morphology and device performance in nonfullerene PSCs based on a series of nonfullerene donor-acceptor pairs. This shows that optimal combination of photovoltaic donor and acceptor pairs with complementary absorption, well-aligned frontier energy levels, and well-intermixed crystalline morphology can provide great potential to further increase the power conversion efficiency of nonfullerene solar cells to exceed fullerene-based devices.

Sensitizing Triplets with Metalloporphyrins and Metalloidoporphyrins

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The molecular singlet state S_1 is easy to excite and observe, but is too short lived to store energy. Triplet states, however, are stable on the microsecond scale or longer. We use triplet states as a reservoir of energy to drive quasiparticle scattering processes with applications to solar energy.

For sun-driven photochemical processes, the absorption spectrum of the chemical system is important because it determines the proportion of sunlight that can be captured. We will show how metallation and functionalization of porphyrins modifies the absorption spectrum. To create a triplet state, it is necessary to induce efficient intersystem crossing. This is typically achieved using spin-orbit coupling in a central heavy atom, such as Pd or Pt. We will use time-resolved fluorescence to show that intersystem crossing also occurs in porphyrins with cheaper light elements occupying the same site. Based on delayed fluorescence and phosphorescence, we report the relationship between the central atom and the triplet lifetime. Finally, we show that, when the triplet state is quenched by energy transfer to a useful photochemical process, the quenching rate constant is sensitive to the choice of central atom

Sewage Sludge Heavy Metal Analysis and Agricultural Prospects for Fiji

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Insoluble residues produced in Waste Water Treatment Plants (WWTP) as by products are known as sewage sludge (SS). Land application of SS, particularly in agricultural lands, is becoming an alternative disposal method in Fiji. However, currently there is no legislative framework governing its use. SS together with its high nutrient and organic matter contents, constitutes some undesired pollutants such as heavy metals, which may limit its extensive use. The focus of this study therefore was to determine the total concentrations of Pb, Zn, Cd, Cu, Cr, Ni and Mn in the SS produced at the Kinoya WWTP (Fiji) and in the non-fertile soil amended with the SS at 20, 40, 60, 80% application rates and in the control (100% Soil). The bioavailable heavy metals were also determined as it depicts the true extent of metal contamination. The treatment mixtures were then used to cultivate cabbage plants in which the total heavy metal uptake was investigated. Total Zn (695.6 mg/kg) was present in the highest amounts in the 100% SS (control), followed by Pb (370.9 mg/kg), Mn (35.0 mg/kg), Cu (65.5 mg/kg), Cr (20.5 mg/kg) and finally Cd (13.5 mg/kg) and hence a similar trend was seen in all treatment mixtures. The potential mobility of sludgeborne heavy metals can be classified as Ni > Cu > Cd > Zn > Mn > Cr > Pb. Total metal uptake in plant leaves and stems showed only the bioavailable metals Cu, Cd, Zn and Mn, with maximum uptake occurring in the leaves. Ni, despite being highly mobile was not detected, due to minute concentrations in the SS treatments. Optimum growth occurred in the 20 and 40% SS treatments. However maximum Cu and Mn uptake occurred in the 40% SS treatment thereby making the 20% treatment the most feasible. Furthermore the total and bioavailable metal concentrations observed were within the safe and permitted limits of the EEC and USEPA legislations.

Silk-heme CNT Biosensor for Sensitive Detection of Nitric Oxide

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Due to its biological and environmental importance, nitric oxide (NO) detection has attracted the focus of many researchers worldwide especially aiming to detect it at the micro or submicromolar levels. Despite the variety of sensors designed for NO detection, the electrochemical ones attract special attention due to a number of features such as ease of operation, low cost and ability to miniaturise and hence adaptability for use in field and point of care analysis. This work involved the design of an electrochemical NO sensor using a two layer assembly comprising Silk-heme film adhered onto a multiwalled CNT (MWCNT) modified electrode. Heme based sensors have been used before, though most of them rely on NO detection by oxidation which makes them susceptible to interferences. The other problem is the stability of these heme based sensors where most suffer from limited operational stability. The unique combination of our NO sensor involving the strong interaction between heme and silk and heme/silk and MWCNT led to the design of an extremely stable sensor which showed retention of more than 86% of initial response after two months of operation. Besides that, the sensor showed high sensitivity with a LOD of 2 nM, excellent selectivity in presence of different interfering species and good linearity from 19 nM to 190 nM. In addition, the presence of heme and MWCNT enabled low potential detection of NO by electrochemical reduction at -0.75 V in a pH 3.0 buffer solution in presence and absence of oxygen.

SINGLE ENTITY ELECTROCHEMISTRY: AN ELECTROANALYTICAL PERSPECTIVE

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ABSTRACT

A whole host of new electrochemical techniques have been employed to perform experiments on single cells, single nanoparticles, single features in composite materials and even single molecules. This different techniques have certain unifying features, such as the measurement being performed predominantly near-field, which allows them to be classified together as single entity electrochemistry. The majority of these studies have then used these techniques to provide fundamental mechanistic information about the behaviour of single entities as distinct from ensembles of entities. Single entity measurements of course have tremendous application in electroanalysis as detecting single entities not only means devices have the ultimate detection limit of one thing, but also the ability to detect many single entities allows analytical information to be achieved without calibration by counting.

In this presentation new approaches from our laboratory for detecting rare molecules and rare single cells will be outlined, both of which can be regarded as single entity electrochemistry measurements. In the first approach solid state nanopores combined with magnetic nanoparticles as a solution to the issue of nanopores being able to detect single molecules but with low concentrations the response times are very low. This will be illustrated *via* the detection of the protein, prostate specific antigen. In then second approach the ability to capture and release single rare cells will be demonstrated. This is achieved using a semiconducting electrode modified with an electrochemically cleavable unit and antibodies selective for a given cell type. By having the semiconducting electrode in depletion, the electrochemical cleavage will only occur where the electrode is illuminated. In this way, single cells can be released while leaving all other cells on the surface.

SINGLET FISSION AND TRIPLET FUSION FOR SOLAR ENERGY CONVERSION

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A solar photovoltaic energy conversion device with a single energy threshold is limited to an efficiency of about 33% under the standard solar spectrum. The two dominant loss mechanisms which must be addressed when considering how to improve the energy conversion efficiency of a single threshold solar cell are: The lack of absorption below the threshold; and the thermalization of carriers to the band edge following absorption of high energy photons. Molecular electronic states can be exploited to address these efficiency losses.

Photochemical upconversion is a process which addresses the absorption of low energy photons. For several years, we have been developing chemical compositions which absorb low energy photons to generate a high concentration of triplet states. When the triplet states annihilate in a material with a large singlet-triplet splitting, e.g. rubrene, excited singlets are produced which radiate higher energy photons. This process, also known as triplet fusion, has been applied to a variety of solar cells.

Singlet fission is a process whereby a material absorbs a higher energy photon to generate singlet states which undergo decay to a multi-excitonic states consisting of two triplets. If the energy of the triplets can be efficiently harvested, then a solar cell could exceed the 33% limit. We showed that such a solar cell operates most efficiently where the fission is endothermic, such as in tetracene. I will discuss the mechanism of singlet fission and triplet fusion in the light of time-resolved photoluminescence experiments.

Singlet Fission of TIPS-Pentacene in a Host Polymer Matrix

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Singlet fission is a process by which a singlet exciton is dissociated to form two triplet excitons in a spin allowed fashion within a pair of molecules. Singlet fission is attracting significant interest in renewable energy research because it addresses a critical issue in single-junction solar cells, of which the efficiency is limited to ~33%. Singlet fission solar cells can potentially minimise thermalisation of the initially prepared exciton, leading to a theoretical efficiency limit of 45%. Owing to the requirement of proximity of the two molecules for singlet fission, the intermolecular distance is expected to play a significant role in the quantum yield of triplet excitons. This issue, however, has not been addressed in singlet fission research thus far. In this work, the development of an aqueous nanoparticle system in which TIPS-pentacene, a compound that is known to undergo efficient singlet fission, in an inert, amorphous host polymer matrix will be presented. By tuning the TIPS-pentacene/host polymer concentration ratio, the average intermolecular distance of TIPS-pentacene can be varied. We have employed a combination of femtosecond transient absorption and time-resolved fluorescence spectroscopy to study the TIPS-pentacene/host polymer nanoparticles. The relaxation dynamics of excited state TIPS-pentacene exhibit a strong dependence on intermolecular distance, indicating a control of processes including singlet fission and triplet recombination.

Small Molecule Microarray (SMM)-Based Discovery of PARP14 Inhibitors

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ABSTRACT TEXT

Poly(ADP-ribose) polymerases (PARPs) are key enzymes in a variety of cellular processes. Most small-molecule PARP inhibitors developed to date have been against PARP1, and with poor selectivity. PARP14 has recently emerged as a potential therapeutic target, but its inhibitor development has trailed behind. Here we describe a small molecule microarray-based strategy for miniaturized high-throughput synthesis, screening of > 1,000 potential bidentate inhibitors of PARPs, and the successful discovery of until now the most potent PARP14 inhibitor **H10** (IC50 = 0.49 μM) with > 20-fold selectivity over PARP1. Co-crystallization of the PARP14/**H10** complex indicated **H10** bound to both the nicotinamide and the adenine subsites, which revealed that **H10** is the first bidentate inhibitor of mono (ADP-ribosyl) transferases (m-ART). Further structure-activity-relationship studies identified important binding elements in the adenine subsite. In tumor cells, **H10** conferred moderate cellular activities to chemically knockdown endogenous PARP14 activities.

Soft Matter Enabled Nanomedicines

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ABSTRACT:

Synthetic functional materials designed specifically to respond to biological cues are the subject of intense research interest due to their possible application in drug delivery. These "smart" materials offer not only new avenues for overcoming some of the current limitations in drug delivery via nanomedicines, but also open pathways to new treatment strategies. I will highlight our current research in the following areas:

A) **Improved Subcellular Targeting:** Novel polymers which respond to biochemical differences between the extra-and intracellular environments are useful for preparing particles which can chaperone a therapeutic agent in the systemic extracellular environment, and release said agent only when the particle is internalized by a target cell and in a specific sub cellular location. For example, the specific subcellular targeting of the NK1 internalized receptor signaling complex in spinal neurons shows promise as a new treatment for chronic pain and itch.

B) **Exploiting Cell Communication Pathways:** Developing new materials which can specifically interact with or recruit cell communication pathways, for example those involving gasotransmitters (nitric oxide, hydrogen sulfide etc.), offer unique opportunities for improving therapeutic outcomes in cancer treatment. We are particularly interested in improving the chemotherapy treatment of chemoresistant cancers by developing materials which switch off cellular efflux pumps.

C) **Designed Biomimetic Polymers:** Translating the functional motifs of antibacterial lipopeptides to synthetic polymers opens new approaches for addressing the increasing global concern of drug resistant bacteria. We have developed new synthetic antibacterial peptide analogues that exhibit broad spectrum antibacterial activity using the latest polymer synthesis techniques.

Solvent effects on the excited state characteristics of adenine-thymine base pairs

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

The ability of dissipating the electronic excitation and thus preventing the photo-induced damages and providing natural protection and photo-stability is, perhaps, the most significant characteristic of DNA bases as the building block of life on Earth. Therefore, it is reasonable that the study of excited states of DNA bases has attracted remarkable research interest. The challenge of the experimental study of DNA photo-physics stems from the intrinsic complexity of dynamical behaviours of the excited states. In this regard, the quantum mechanical methods for the study of excited electronic states are providing helpful insight. In this study, we apply time dependent density functional theory (TDDFT) to analyse the excited states of DNA base-pair adenine-thymine in both canonical Watson-Crick and stacked configurations. The excited state wavefunctions are analysed and visualized in terms of one-electron transition density matrix (1TDM), and natural transition orbitals. The environmental effect on the excited states is considered using the non-empirical effective fragment potential method. The extent of de-localization and the charge transfer character of excited states in near- and far-ultraviolet region of electromagnetic spectrum are identified. It is also shown that the environmental effect on the de-localization is significant and it varies with the configurations. Additionally, localized Frenkel type states, as well as de-localized states involving multiple molecular fragments, are also identified.

Solvent Nanostructure, the Solvophobic Effect and Amphiphile Self-Assembly in Ionic Liquids

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The ability of ionic liquids (ILs) to support amphiphile self-assembly into a range of mesophase structures has been established as a widespread phenomenon. From the ILs evaluated as self-assembly media, the vast majority have supported some lyotropic liquid crystal phase formation. Many neat ionic liquids have been shown to segregate into polar and non-polar domains to form a nanostructured liquid. A very strong correlation between the nanostructure of the ionic liquid and its characteristics as an amphiphile self-assembly solvent has been found. In this presentation, we discuss ionic liquids as amphiphile self-assembly media, and identify trends that can be used to distinguish which ionic liquids are likely to have good promotion properties as self-assembly media. In particular these trends focus on the nanostructure of neat ionic liquids, their solvent cohesive energy density, and the related solvophobic effect. We forecast that many more ILs will be identified as amphiphile self-assembly solvents in the future.

Solving the Redundant Coordinate Problem

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At any given geometric configuration of an *N*-atom molecule there are 3*N* – 6 linearly independent local coordinates. To describe the molecule at *any* point in configuration space, however, we must use a redundant coordinate description, describing the molecule in terms of some set of primitive redundant coordinates. Such descriptions are used in the optimization routines available in electronic structure codes and in descriptions of global molecular potential energy surfaces. For *normal* molecules, for example methane, CH_4, the ground vibrational state *can* be described using 3*N* – 6 local coordinates from this set– for example, the CH_4 normal coordinates. This choice, however, is particularly problematic for the protonated water dimer, $H_5O_2^+$: even large sets of primitive redundant coordinates suffer from linear. Here we introduce a general solution to the redundant coordinate problem and demonstrate that it can be used to develop accurate interpolated molecular potential energy surfaces. We assess our potential energy surface using quantum diffusion Monte Carlo (QDMC) simulations of the $H_5O_2^+$ ground state, determining its quality of in terms of (i) a test set of configurations (ii) the number of QDMC walkers “killed” as a result of artefacts in the potential, (iii) the $H_5O_2^+$ zero-point energy and (iv) approximate $H_5O_2^+$ anharmonic vibrational frequencies. In particular, our solution to the redundant coordinate problem enables us to retain inverse atom-atom distances as primitive redundant coordinates, with a number of inherent advantages. Moreover, our strategy is generally applicable to *any* case where redundant coordinates are used to describe a system.

Spatial Control of Self-assembly in Photo-sensitive Block Copolymers

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Block copolymers can self-assemble into well-defined, nanoscale morphologies, which are typically isotropic and lack long range order. Chemical or physical templates generated through optical lithography can direct self-assembly to create morphologies with enhanced long range order and fashion them into hierarchical patterns. This allows the patterns to be optimized for a desired application. Alternatively, stimuli-responsive polymers have the potential to exert similar control over long range order and pattern complexity. Here, photo-responsive block copolymers are synthesized and the relationship between light induced changes in their chemical structure and their self-assembly behavior is investigated. This will allow direct spatial control to be exerted over self-assembled nanostructures produced in thin block copolymer films.

Poly(benzyl methacrylate)-b-poly(o-nitrobenzyl methacrylate) was synthesized through Reversible Addition-Fragmentation Chain-transfer polymerisation and successive post-polymerisation modification reactions. When the o-nitrobenzyl group is exposed to ultra-violet light, it degrades to reveal a carboxylic acid functional group. Following UV exposure of a thin film of this polymer, solvent vapour annealing is used to develop the material's morphology. Selection of a good solvent for the protected polymer allows microphase separation into well-defined nanoscale domains in unexposed areas, resulting in the formation of islands and holes. If this solvent is also a poor solvent for the deprotected polymer then island and hole formation is inhibited in exposed regions. Finally, we use a mask we selectively irradiate certain areas of the surface and demonstrate both the spatial selectivity of this process and that confinement of island and hole structures enhances control over their topography.

SPECIATION ANALYSIS OF MERCURY AND METHYLMERCURY USING METAL ORGANIC FRAMEWORKS

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The toxicological and biological effects of mercury (Hg) species highly depend on their chemical forms. For instance, methylmercury (MeHg+) have much more harmful effects than inorganic Hg, for its higher toxicity, easy bioaccumulation and volatility. Therefore, effective speciation analysis of Hg is more important than the determination of total Hg. During the past several years, metal-organic frameworks have become more attractive because of its excellent properties. In this work, we developed a facile method using MOFs nanoparticles of ZIF-7 and ZIF-60 for speciation analysis of inorganic mercury and methylmercury. ZIF-7 and ZIF-60 were synthesized using microwave-ultrasound assisted method, with short reaction time, easy procedure, and small particle size obtained. Based on strict cavity confinement of the ZIF-7 and ZIF-60 nanostructures, the proposed method exhibited excellent selectivity for both Hg(II) and MeHg+, and could be used for the determination of aqueous Hg(II) and MeHg+, respectively, in a fast and sensitive manner.

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STANDARDIZATION OF MEDICINAL PLANTS USING 13C NMR AND MULTIVARIATE METHODS

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ABSTRACT

A method for the chemical profiling and chemical standardization of medicinal plants using 13C nuclear magnetic resonance (NMR) and chemometric analysis of the chemical shift data is described using *Vitex negundo* as an example. The chemical profile was obtained using a k-means cluster profile and chemical standardization which was achieved using a multivariate control chart. *V. negundo* samples were made up of four groups: the training set, submitted samples from production farms, commercial samples, such as tablets, capsules and teas, and experimental samples (samples which were allowed to degrade). Four groups were generated by k-means cluster, which generally corresponded to the four types of samples. The multivariate control chart identified samples whose profile exceeded the upper control limit; these were identified as commercial and experimental samples. The samples were also analyzed by quantitative thin layer chromatography (qTLC). Comparison of the qTLC results with the multivariate control chart showed poor correspondence. This means that a univariate analysis of a plant sample using a single compound is useful only for quantification of the target compound. In conclusion, this work showed that multivariate methods, such as k-mean cluster and multivariate control chart, are more appropriate for multicomponent mixtures such as medicinal plants. Further, 13C NMR was shown to be an effective method for the profiling of medicinal plants.

Stereoregulation in the radical polymerization of methacrylate salts

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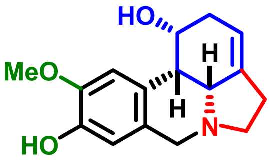
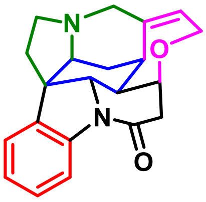
The aim of synthetic polymer chemistry is to precisely construct complex macromolecular species, while maximizing the yield, step-efficiency and cost-effectiveness of the requisite procedures. Much current research has focused on the growing applications stimuli-sensitive 'smart polymers', which can respond to externally induced physical or (bio)chemical stimuli. Over the last few decades, synthetic polymer chemistry has been revolutionized by the discovery and subsequent development of 'living' radical polymerization. Unfortunately, developments in stereocontrol over this period have been much more modest and tacticity is still poorly regulated in many monomer systems. A promising approach is via the use ionic auxiliaries, such as methacrylate salts, which can then be converted to their esters post-polymerization. Depending on the auxiliary and conditions, a wide range of tacticities can be targeted. Building on the experimental work of Kadokawa and co-workers (*Macromolecules*, 2008, **41**, 489-492), we have been using theory and experiment to explore the mechanism of tacticity regulation in these systems and improve both the control and the subsequent post-polymerization reactions. This talk will outline our recent advances in the stereocontrol of methacrylate salts.

Stereoselective Total Synthesis of Alkaloids and Towards a Functional Protecting Group Approach

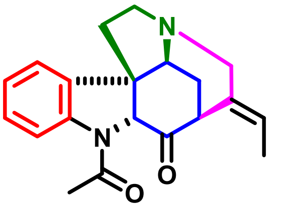
Total synthesis or the complete chemical synthesis of a complex natural product has elicited substantial interests in the scientist community during the last century. A milestone has been reached in 1954 when Woodward and coworkers described the first synthesis of Strychnine. This science has mainly evolved due to the diversity of novel synthetic tools often discovered to solve a problem in total synthesis. Nowadays a thoughtful synthesis has to be concise, asymmetric and environmental benign. In this lecture, total synthesis of alkaloids such as (-)-fortucine, (-)-strychnopivotine or strychnine mediated by hypervalent iodine reagents will be discussed. Furthermore, preliminary results towards the development of a "functional protecting group" will be presented. This method is envisaged as an alternative to the free protecting group strategy, which is often difficult to implement when dealing with challenging polyfunctional molecules. A "functional" protecting group is one, which not only masks the reactivity of a sensitive ensemble but it also carries a moiety of the final target, which will be transferred to the substrate at the time of deprotection. This atom economical avenue requires only slightly thermic and basic conditions, releases simple by-product and enables the rapid formation of carbocycles and heterocycles present in alkaloids. An extension to these approaches to stereoselective cycloaddition processes will be described.



(-)-Fortucine



Strychnine



(-)-Strychnopivotine

Structural Investigations of Ionic Liquid Mixtures

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The structures of ionic liquids (ILs) are remarkably complex due to the interplay between strong Coulombic forces, other electrostatic interactions such as hydrogen bonding, and weaker dispersive forces including π-π stacking.[1, 2] _ENREF_1 Despite this structural complexity, the majority of mixtures of ILs exhibit nearly ideal behaviour, allowing their physical properties to be predicted with reasonable accuracy from those of the simple IL constituents.[3, 4] Nonetheless, the detail of the structural changes that occur as ILs are mixed remains unresolved, particularly with respect to the existence and magnitude of preferential interactions between specific ion sites within these mixtures. For example, it has been argued there are strong preferences for anions to occupy specific locations around a common cation,[5] that similarly charged ions are randomly mixed regardless of their atomic arrangement,[6] and that there are no preferential hydrogen bonding interactions between different ions.[7] These findings are difficult to easily reconcile.

Towards gaining greater insight into the structural changes that occur as ILs are mixed, we have conducted a detailed study of IL mixtures using NMR spectroscopy both of the neat ILs and of the ILs diluted by dichloromethane-d_2 in conjunction with molecular dynamics and quantum chemistry calculations.[8] This presentation will outline the effect of forming mixtures of 1-butyl-3-methylimidazolium ($[C_4C_1im]^+$) ILs with different anions on structural features such as charge ordering, hydrogen bonding, π-π stacking and anion-π interactions. The impact of these structural features on the physical properties of these mixtures and the coherence of these findings with the literature will be discussed.

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STRUCTURE AND CYTOTOXICITY OF THE GREEN SEAWEED ORIGINATED ULVAN

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ABSTRACT TEXT

Ulvans are water-soluble sulfated polysaccharides derived from marine green seaweed. They were reported to exhibit a wide range of physiological and biological activities. The structural complexity of ulvans may be derived from the differences in seaweed species, extraction method and place of cultivation [1-3].

This work presents an investigation on the structure of ulvan obtained by water extraction from the green seaweed *Ulva lactuca* by using IR, NMR, SEC-MALL and ESIMS methods. The results showed that the ulvan with a molecular weight of 347000 was composed of rhamnose (Rha), galactose (Gal), xylose (Xyl), manose (Man), glucose (Glu),with a mole ratio of 1 : 0.03 : 0.07 : 0.01 : 0.06, respectively. The uronic acid and sulfate content in the ulvan was found to be at 21.5% and 18.9%, respectively. This ulvan mainly consists of disaccharide [→4)-β-D-GlcA-(1→4)-α-L-Rha3S-(1→] and other minor disaccharide β-GlcA-(1→2)-α-Xyl and β-GlcA-(1→2)-α-Rha. The ulvan was further evaluated for its cytotoxic effects on three human cancer cell lines and shown a significant cytotoxicity against the hepatocellular carcinoma (IC$_{50}$ at 29.67±2.87 μg/ml), human breast cancer (IC$_{50}$ at 25.09 ±1.36 μg/ml), and cervical cancer (IC$_{50}$ at 36.33±3.84 μg/ml) in a dose dependent manner. The ulvan was shown a potential natural product as anti-cancer compound and will be further developed in our future work.

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Structuring Of Food Emulsions – Colloidal Pathways For Controlling Product Properties

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A simple consideration of colloidal structuring in foods is the requirement to impart physical stability for food systems comprising immiscible components such as oil, water and air. However, it is recognised within the modern food manufacturing industry that the ability to control colloidal interactions and assemblies within a food structure provides a means for modifying a range of product attributes, e.g. material properties, technical functionality, sensory behaviour and even the way in which such foods are digested.

This presentation will aim to exemplify the consequences of colloidal interactions on the properties of two particular emulsion based foods. Firstly, highlighting how specific interactions, such as depletion forces, can negatively compromise the stability of fluid emulsions, using dairy based beverages as an example. In ascertaining the factors contributing to the depletion effect, it will be shown how formulations can be iteratively adjusted to mitigate against such instabilities.

Secondly, the presentation will seek to demonstrate how controlled destabilisation of emulsion systems can be effected to enable improvements in material and functional behaviours as applied to soft solid foods. In this context, it will be shown how manipulation of the interactions between dispersed and continuous phases during processing of a Mozzarella cheese can lead to particular structural outcomes that, in turn, can greatly influence product properties such as melt, flow and oil release during heating.

These examples provide a pertinent overview of how structural manipulation of the colloidal state in foods can be utilised in the development of products with enhanced value.

STUDIES INTO THE CHEMICAL AND PHYSICAL PROPERTIES OF LATENT FINGERMARKS

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Despite the numerous studies reported in recent years, significant challenges remain in the effective development of latent fingermarks, which demand further investigations into fingermark chemistry. Key objectives of the studies that investigated the compositional variation of latent fingermarks over time include; (i) identification of compounds which remain stable over time (or are stable degradation products) as potential targets for fingermark development, (ii) establishing linkages between individual traits and fingermark composition and (iii) development of fingermark dating techniques. To date, aside from some broad trends observed, establishing any significant correlations within this context has been incredibly challenging due to the complex nature of the deposit itself and also due to inter- and intra-donor variation of the chemical composition. [1]

Here we present further investigations into latent fingermark composition and its variation as a function of time, elaborating challenges posed to current lines of research. This includes a detailed study of the protocols for sampling and subsequent preparation of latent fingermark specimens for chemical analysis. Various analytical instrumentation including atomic force microscopy [2], synchrotron sourced FTIR microscopy, gas chromatography-mass spectrometry and liquid chromatography-high-resolution mass spectrometry were utilised in this study. The findings of this work will enable a more evidence-based approach for ex-situ and in-situ investigations of latent fingermark composition.

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Sub-Doppler Two-Photon-Excitation Spectroscopy Of Atomic And Molecular Rydberg States

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ABSTRACT TEXT

A versatile pulsed laser-based system has been developed for high-precision spectroscopic applications in the deep ultraviolet (UV) region where high peak power and narrow optical bandwidth are needed. This all-solid-state nonlinear-optical light source generates tunable narrowband 25-ns single-longitudinal-mode pulses in the near-infrared wavelength range of 820–850 nm. This pulsed radiation is amplified and upconverted to yield coherent tunable UV radiation for sub-Doppler two-photon excitation (TPE) spectroscopy in the fourth-harmonic wavelength range of 205–213 nm. We have already used this system for sub-Doppler UV TPE studies of gaseous atoms: krypton (Kr) at ~212.5 nm [1] and xenon (Xe) at 205–213 nm [2,3]. The latter investigations have resolved diverse isotope shifts and hyperfine structure for 33 high-energy Rydberg states of Xe [2]; individual isotopic contributions have been separated in more recent mass-selective measurements [3]. Our ongoing research focuses on UV TPE spectra for Rydberg states of molecular oxygen (O_2) at ~210 nm, where rotational structure and/or predissociation-rate linewidth effects are relevant to atmospheric and environmental science.

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SUPER-RESOLUTION MICROSCOPY COMING OF AGE: FROM CONCEPTS TO BIOMEDICAL APPLICATIONS

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ABSTRACT TEXT

Super-resolution microscopy by single-molecule photoactivation or photoswitching and position determination (*localization microscopy*) has the potential to fundamentally revolutionize our understanding of how cellular function is encoded at the molecular level. Among all powerful high-resolution imaging techniques introduced in recent years, localization microscopy excels at it delivers single-molecule information about the distribution and, adequate controls presupposed, even absolute numbers of proteins present in subcellular compartments. This provides insights into biological systems at a level we are used to think about and model biological interactions. We briefly introduce basic requirements of localization microscopy, its potential use for quantitative molecular imaging, and discuss present obstacles and ways to bypass them. We demonstrate the advantageous use of *d*STORM for quantitative imaging of synaptic proteins, the study of plasma membrane organization, and the molecular architecture of multiprotein complexes. Finally, we outline how *d*STORM can be used advantageously to improve next generation medical therapies.

Supramolecular Hydrogels Based on Poly(methyl vinyl ether -alt-maleic acid)

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ABSTRACT

Novel supramolecular hydrogels can be formed from azobenzene (or adamantane) grafted poly(methyl vinyl ether-alt-maleic acid) (PMVE-alt-MA) (P(MVE-alt-MA)-g-Azo (or Ad)) (guest polymer) and *β*-cyclodextrin grafted (P(MVE-alt-MA)-g-β-CD) (host polymer) respectively. The host and guest polymers interact mainly via inclusion complexes between trans-azobenzene (or adamantane) groups and cyclodextrin cavities. These hydrogels are intelligent. The supramolecular hydrogel (P(MVE-alt-MA)-g-Azo/P(MVE-alt-MA)-g-β-CD) are sensitive to both light and heating, and supramolecular hydrogel (P(MVE-alt-MA)-g-Ad/P(MVE-alt-MA)-g-β-CD) is self-healing, as shown by rheological properties. Using these intelligent hydrogels as cell scaffold, we tried to culture ovarian cancer cells. These smart hydrogels provided a good platform to study the behavior of ovarian cancer cells.

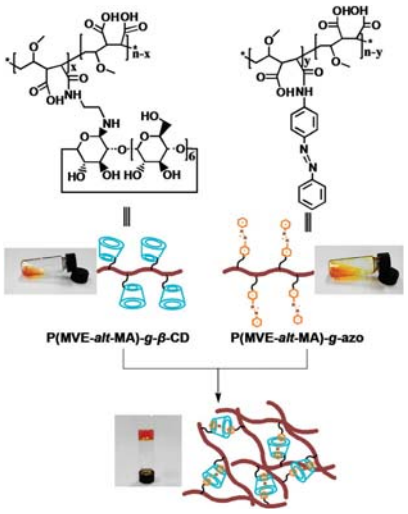

Figure 1. Assembly of host polymer P(MVE-alt-MA)-g-b-CD and guest polymer P(MVE-alt-MA)-g-azo. Photographs of mixtures of host-guest polymers before a) and after b) UV irradiation.

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Surface Engineering for MedTech and BioTech Applications

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ABSTRACT

The ability to control interactions between biomolecules and surfaces can influence a widely divergent number of Medical and Bio-Technology applications. We want to immobilize proteins on biosensors but ask them to behave as they would in the body, stimulate cells to assemble tissues, form new blood vessels and replicate structures in the lab just as well as they can in our bodies. We want methods that prevent bacteria forming biofilms and better still we would like them to stop attaching to surfaces full stop.

This range of applications presents challenge in terms of both surface modification methods and the sensitivity of techniques we use to characterize these systems. This talk will explore the challenges of developing polymeric surface modification strategies for applications ranging from wound dressings and nerve tissue engineering through to microfluidics for shotgun proteomics and surfaces that mimic the behaviour of the cell membrane. At the heart of this work is the need to develop approaches to characterising these materials by combining physical and chemical characterisation techniques with biochemical assays and imaging to gain insight into the performance of the materials.

Surface modification for smarter materials: from graphene to magnesium

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This presentation will describe some of our recent work aimed at extending our surface modification methodologies towards problems in energy storage and biodegradable medical implants.

Graphene has the highest theoretical capacitance of any material which suggests it should be the material of choice for supercapacitors. However its theoretical capacitance is never realised in experimental systems. One issue is the aggregation of graphene sheets which decreases the total exposed surface area. Our approach to preventing this aggregation and thereby optimising the capacitance, is to introduce covalently attached spacers using aryldiazonium ions.[1] We have established modification conditions that do not decrease the capacitance of single few layer graphene (FLG) sheets, and at the same time, ensure that the per-sheet capacitance remains constant as the stack is built up.

In the area of biodegradable medical implants, magnesium is a prime candidate for orthopaedic applications thanks to its mechanical properties and lack of biotoxicity. However, its biocorrosion rate must be slowed to allow tissue regrowth and to avoid build-up of hydrogen gas around implants. Surface coatings may address these problems, but to date, poor adhesion is a common failing. In preliminary work we have established that reaction of magnesium with aryldiazonium ions gives strongly adherent coatings which decrease the corrosion rate. In ongoing work we are investigating the use of these layers to improve the adhesion of bioactive polymer coatings, via covalent or non-covalent interactions.

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SURFING THE SULFATE WAVE: NEW CHEMICAL AND ANALYTICAL TOOLS TO STUDY SULFATE ESTER DRUG METABOLITES

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Sulfate ester metabolites are rapidly growing in importance in the field of anti-doping analysis. It has been known for many years that the formation and subsequent decomposition of phase II sulfate conjugates is involved in the generation of epimerised 17β-alkyl-17α-hydroxy steroids and other minor but significant metabolites. However, more recent studies have shown that monitoring phase II sulfate conjugates can increase detection windows for some analytes, and in several cases, sulfate metabolites can be used to distinguish between endogenous and exogenously administered steroids.

This presentation will discuss advances in the chemical and enzymatic synthesis of sulfate ester reference materials, including labelled derivatives, and how they can be used to develop new analytical methods such as Constant Ion Loss (CIL) Mass Spectrometry (MS) for the untargeted detection steroidal bis(sulfate) metabolites. The development of engineered enzymes for the hydrolysis of steroid sulfate metabolites will also be described. Together these methods significantly augment the tools available to analytical chemists for the study sulfate ester metabolites. Results on the application of these methods in anti-doping analysis and the pre-natal clinical diagnosis of diseases such as Smith–Lemli–Opitz Syndrome (SLOS) or cytochrome P450 OxidoReductase Deficiency (PORD) will be presented.

Symmetry breaking, $AgNO_3$, and Aspect Ratio in Gold Nanorod Growth

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Single crystal gold nanorods have attracted much attention due to their tuneable optical properties, which are dependent on the nanorod aspect ratio (length/width). The aspect ratio is able to be controlled by varying $AgNO_3$ concentration.[1] However, the role of $AgNO_3$ during the growth stages in which symmetry breaking occurs and in control of the aspect ratio during subsequent nanorod growth is an outstanding question. We define symmetry breaking as the removal of a symmetry element from the symmetric cuboctahedral seeds. Here we report our investigation into the role of silver nitrate on the symmetry breaking of nanocrystalline seeds and its influence on the aspect ratio of gold nanorods. The seeds are overgrown in the presence of silver nitrate to the size range within which symmetry breaking occurs.[2] Electron microscopy analysis reveals the overgrown seeds are predominantly single crystalline. Further size analysis shows the symmetry breaking occurs only between 4 nm to 6 nm.[2,3] Furthermore, the size of the crystals at the symmetry breaking point decreases with decreasing [$HAuCl_4$]:[$AgNO_3$] ratio.[3] The effect of the symmetry breaking on the following rod growth is studied by step-changes to the $AgNO_3$ concentration throughout the symmetry-breaking period. It is found that the symmetry breaking size determines the final nanorod width, while the length depends on the gold concentration in the growth solution. These results fully elucidate the role of silver nitrate in symmetry breaking of gold seeds and, in turn, on the final width and aspect ratio of the gold nanorods.[3]

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Synthesis and single crystal structure of pillar[5]arene-based metal organic frameworks

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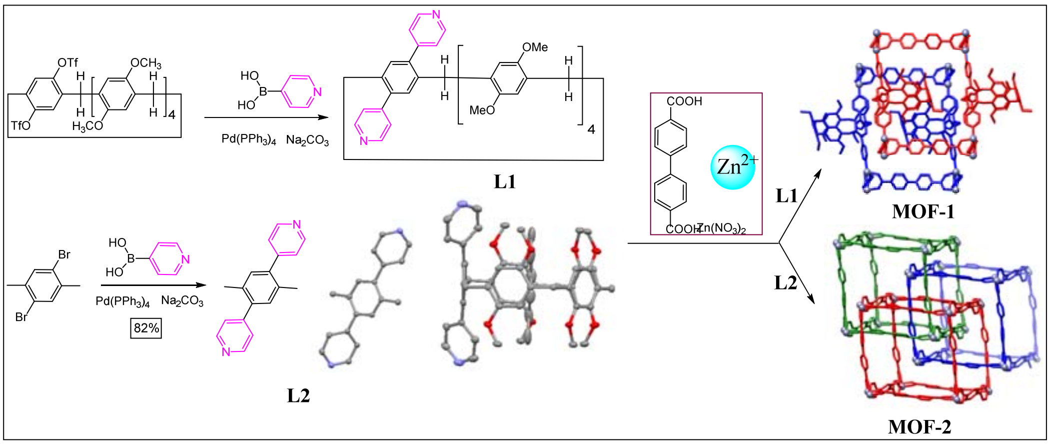
Macrocycle-based metal-organic frameworks (MOFs) have opened up the possibility of forming hierarchically porous materials with two levels of porosity: one from the framework itself and the other from the macrocycle components. This class of hybrid materials, which has the potential to bring out novel properties, has attracted considerable interest in the fields of materials science and supramolecular chemistry.[1] Among the many types of macrocycles, pillararenes have become 'star' molecules since they were first reported by Ogoshi et al in 2008.[2] To date, Strutt et al. have reported the only example of a pillararene-based MOF;[3] however, the single-crystal X-ray data were not obtained on account of the disorder from the rotational freedom of pillar[5]arene. Herein, we report the first crystal structure of pillararene-based **MOF-1**, the model **MOF-2** (lacking pillararene) was also prepared for comparison. The synthetic route and the crystal structures of **MOF-1** and **MOF-2** are depicted in **Scheme 1**.



Scheme 1. Synthesis and crystal structures of pillar[5]arene-based MOFs

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Acknowledgement

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The Synthesis of 6,6,6-trifluoro-L-fucose as a Metabolic Inhibitor of Fucosyltransferase 8

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Monoclonal antibodies (mAbs) are targeted immunotherapeutic agents and represent the largest class of biologics in clinical use. Antibodies used in oncotherapies commonly work by binding to cancer-specific antigens on the cell surface and recruiting effector cells, like natural killer cells, to induce antibody-dependent cellular cytotoxicity (ADCC). The therapeutic potency of mAbs is dependent on the type of N-glycosylation on the antibody's crystallisable fragment (F_c). The IgG1-F_c homodimer is N-glycosylated on a conserved asparagine residue (As297) by a complex-type biantennary glycan[1]. Fucosylation of the IgG1-F_c N-glycan, mediated by fucosyltransferase 8 (FUT8), diminishes the affinity of the antibody for the immunoglobulin receptor FcγRIII on effector cells and so fucosylated antibodies are less effective at inducing ADCC than non-fucosylated antibodies[2]. Inhibitors of FUT8 can be used to manufacture more effective mAbs and may also be used for enhancing the efficacy of antibodies produced by patients against cancer cells.

The glycosylation reaction catalysed by FUT8 involves a GDP-L-fucose substrate and a transition state with significant positive charge delocalized across the anomeric carbon and endocyclic oxygen. Placing an electron-withdrawing group adjacent to the endocyclic oxygen drastically increases the energy of this transition state, preventing the glycosylation reaction. This can be achieved by replacing the methyl group of L-fucose with the strongly electron-withdrawing trifluoromethyl group, to give 6,6,6-trifluoro-L-fucose **(1)**. Endogenous metabolic enzymes convert **(1)** to GDP-6,6,6-trifluoro-L-fucose, a competitive inhibitor of FUT8. We describe an efficient new synthetic route to **(1)**, which produces the desired product in just eight steps from inexpensive D-mannose in 26% yield.

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SYNTHESIS OF HEPARAN SULFATE DISACCHARIDES FOR LC-MS/MS ASSAY DEVELOPMENT

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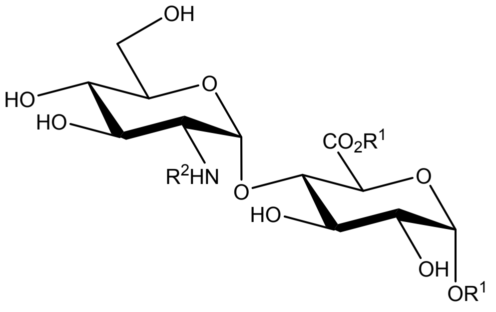
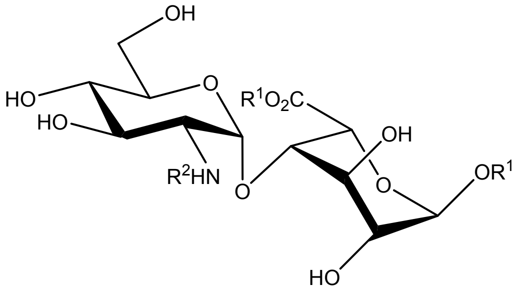
Heparan sulfate (HS) is a highly complex polysaccharide of the glycosaminoglycan (GAG) family that is a marker for a number of diseases, most notably several of the mucopolysaccharidoses (MPS). Quantification of the amount of stored HS in MPS patient samples is important for predicting disease progression for the individual. However, the high degree of structural heterogeneity of HS makes its quantification at physiological concentrations extremely challenging. An LC-MS/MS-based HS assay was developed for measuring HS in MPS urine samples based on depolymerization/desulfation and alkylation of HS via butanolysis or methanolysis, whereby the resultant alkylated disaccharides are quantifiable by LC-MS/MS measurement. Herein we describe the synthesis of HS disaccharides for both butanolysis and methanolysis product identification as well as the synthesis of deuterated disaccharides for use as internal standards in the above assays. The key step of the syntheses for the major species formed from either butanolysis or methanolysis is the glycosylation of a suitably protected di-alkylated uronic acid acceptor with a 2-azido-2-deoxythioglycoside donor promoted by NIS/TMSOTf (or TfOH) to form the desired α-linked disaccharides.



GlcN-GlcA



GlcN-IdoA

R^1 = Bu or Me
R^2 = H or Ac

SYNTHESIS OF NON-NATURAL TIGLIANE SKELETONS: CANCER CELLS SUGGEST...

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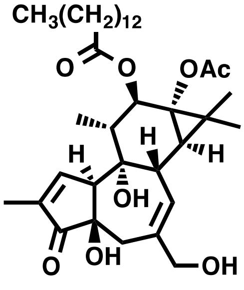
ABSTRACT: Phorbol esters, notably (+)-PMA, have long been used to perturb cell signaling pathways in many normal and disease states (e.g. cancer), but their relative scarcity, and structural complexity, are major barriers to exploiting their potency and selectivity in a mechanistic or therapeutic context. The lecture will detail our successful synthesis of a number of non-natural tiglianes, which has enabled us to postulate an alternate theory on what is really the important structural motif to these potent natural products.



(+)-PMA

Figure 1. Phorbol 12-myristate 13-acetate (PMA), also called 12-O-tetradecanoylphorbol-13-acetate (TPA).

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Synthesis of photo-responsive dynamic polymers using topochemical polymerisations inside nano-spaces

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Topochemical polymerisation has received considerable attention in recent years as an environmentally friendly polymerisation method which can control the stereochemistry of polymer chains. It describes specific monomer crystal to polymer crystal reactions which proceed by UV irradiation or heat. In this research, several thymine derivatives were synthesised and proceed topochemical polymerization in the solid state, in solution state as self-assembly and also inside nanospaces to create photo-responsive dynamic polymers with controlled structure. The design and synthesis of various thymine monomers, determination of monomer crystal structures, self-assembly structure, and characterization of the photoproducts will be discussed in the presentation.

Synthesis of Selective and Perdeuterated Phospholipids for Neutron Studies

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The National Deuteration Facility (NDF) is focused on the provision of deuterated molecules which extends the options for contrast in neutron scattering to encompass not only solvent but molecular deuteration. Over the past few years the NDF has expanded its synthesis capability from simple deuterated fatty acids to complex deuterated molecules including lipids and phospholipids. We are now able to produce head or tail deuterated lipids including phospholipids based on oleic acid with a range of head groups (Fig. 1). These include perdeuterated 1,2-oleoyl-*sn*-glycero-3-phosphocholine (POPC),[1] selectively deuterated POPC, branched chain (phytanic) phospholipids 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine (DPhyPC), and perdeuterated mono oleoyl glycerol and phytanoyl monoethanolamide.[2] These lipids have been extensively used in constructing biologically more relevant model membranes and lipidic matrices for investigations using neutron studies. These include structural and dynamical studies of biomimetic membranes and the encapsulation of biomolecules in lipid-based bicontinuous cubic phases for drug-delivery, membrane protein crystallization, and biosensor applications. Details about design, synthesis and characterisation of these deuterated precursors and final compound will be presented.

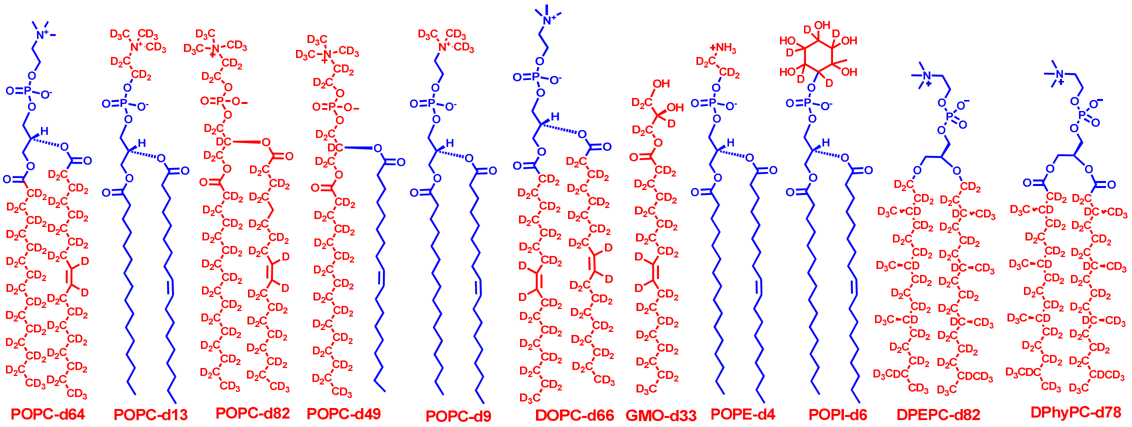

Figure 1: Examples of deuterated lipids synthesised at NDF

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SYNTHESIS OF UHMW ABBA TRIBLOCK POLYMERS USING AQUEOUS RAFT-MEDIATED GEL POLYMERISATION AND CHAIN END MODIFICATION

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Ultra-high molecular weight (UHMW) polymers ($M_n > 1.00 \times 10^6$ g mol^{-1}) are often used in a wide range of industrial processes such as wastewater treatment, mining and minerals processing, oil recovery, hydraulic fracturing and biotechnology. The synthesis of well-defined UHMW polymers using reversible deactivation radical polymerisation techniques remains a challenge and has only been the centre of attention in a limited number of isolated studies. Although UHMW was achieved in these researches, the complexity in architecture has yet to surpass AB diblock polymers. The ability to investigate and develop novel UHMW polymers with more advanced architectures could give rise to a whole new class of materials with unique properties that have the potential to be further implemented in current industrial applications. We hereby report a new synthetic pathway to synthesise UHMW ABBA triblock copolymers using a combination of reversible addition-fragmentation chain transfer (RAFT) polymerisation and chain end modification. A simple two-stage aqueous RAFT-mediated gel polymerisation technique was initially used to synthesise high molecular weight AB diblock copolymers with low dispersities ($Đ < 1.50$). The use of said gel polymerisation method in combination with a redox initiation system allowed for the rapid chain propagation of water-soluble monomers under low reaction temperature (below ambient). These polymers were subsequently used in the final aminolysis stage where the chain end was converted to thiol functionality, which spontaneously couple under oxidative condition to form disulfide bridges between the AB diblock copolymers to produce the final UHMW ABBA triblock copolymers.

Synthetic Efforts Towards Spiroleucettadine

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The rich chemical diversity of marine natural products and their often useful biological activity has provided a wealth of structures that lend themselves to the discovery of potential medicines. Among these interesting structures is spiroleucettadine, isolated from the *leucetta* calcareous sponge by Crews and co-workers in 2004. Initially, an unprecedented [5,5]-*trans*-fused 2-amino-imidazolidine-oxolane structure was proposed and the compound also displayed moderate antibacterial activity (6.25 µg/mL against *Enterococcus durans*).

The disclosure of spiroleucettadine was met with worldwide interest, however several independent efforts towards synthesising the molecule called into question the stability and validity of the proposed structure. Prompted by these results, Crews and co-workers re-evaluated the analytical data and subsequently revised the structure to a [5,5]-*cis*-fused imidazolidinone-oxolane core.

This presentation will focus on our recent efforts to synthesise the revised structure of spiroleucettadine.

Targeted and untargeted analysis of PFAS in Victorian Wastewater

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ABSTRACT TEXT

In Australia Per- and polyfluoroalkyl substances (PFAS) are a contaminant of emerging concern. PFAS have unique properties that make their use in industry and manufacture desirable. However, PFASs are persistent, bioaccumulative and potentially toxic to organisms. Hence, these compounds are important for monitoring and remediation purposes. Traditionally, studies have focused on analysis of a few perflurocarboxylic and sulfonic acids which have been detected in aqueous matrices world-wide. Few studies on newer fluorinated compounds in wastewater and recycled water are available. The occurrence data for alternative classes of PFAS in Australian wastewater is currently unavailable while data for PFCAs and PFSAs is limited. The current study employed unique workflows for the comprehensive analysis and identification of PFASs in two Victorian wastewater treatment plants. Targeted quantification of 15 PFAS was performed using stable isotope dilution on an LC-MS/MS QQQ and LC-QTOF. Further, the samples were screened for the presence of 65 PFASs using a custom database with levels of verification ranging from confirmation of fragments from validated MS/MS spectra to identification of molecular mass and isotope fidelity etc. Finally, software tools such as MassHunter molecular feature extractor (MFE), mass profile professional (MPP) and molecular structure correlator (MSC) were used to propose and identify fluorinated compounds in the water samples not present in the database. The combined targeted and untargeted analysis provides a more complete picture of PFAS contamination in Australian wastewater and recycled water. This study provides additional information to Australian regulatory agencies on point-source PFAS emissions to the environment.

Taxonomy-Guided Microbial Biodiscovery

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Resolution of a microbial culture to the basic taxonomic unit, a species, is often not clear-cut. Strains once considered as robust species have subsequently been shown to be species groups sharing a common phenotype and conserved gene sequences. Increasingly, microbial secondary metabolites are becoming important tools in unravelling microbial biodiversity and taxonomy. As each secondary metabolite is the product of many discrete enzymes, a typical co-metabolite profile represents a significant sub-sample of the functional microbial genome. Comparative analysis of these unique chemical fingerprints offers a rapid and reliable means to identify novel microbial species.

In search of novel Australian Aspergilli, we conducted a survey of forest and scrub soils in the South Burnett Region of Queensland. From the ~200 *Aspergillus* isolates recovered, the phenotype of three strains presented with atypical morphological features with respect to known species in subgenus *Circumdati* section *Circumdati*, and were tagged as putative novel species. Significantly, all three isolates had unique secondary metabolite profiles when searched against our in-house database (COMET) of HPLC-DAD traces from >5,000 known or talented fungal species. This presentation will focus on the chemotype of one of these new species, *Aspergillus hancockii*, isolated from soil in peanut fields near the town of Kumbia. When cultivated on rice as an optimal substrate, *A. hancockii* produced an extensive array of 69 secondary metabolites. Eleven of the 15 most abundant secondary metabolites, constituting 90% of the total area under the curve of the HPLC trace of the crude extract, were novel.

TEMPERATURE RESPONSIVE POLYMERS IN MINERAL PROCESSING

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ABSTRACT TEXT

Temperature-responsive polymers can be reversibly switched between acting as dispersants and flocculants for mineral particles. When adsorbed onto particles' surfaces, such polymers can reversibly switch the contact angle of water on the surface between hydrophilic and hydrophobic. Reagents based on poly (N-isopropyl acrylamide) have been investigated. The polymer switches behaviour above and below the Lower Critical Solution Temperature (32°C). Selectivity for particular mineral surfaces can be controlled by co-polymerisation with a moiety with particular affinity for the surface. Acrylic acid functionality has been used to target iron ores and xanthate functionality has been used to target copper sulphide ores. Both batch sedimentation and continuous lab-scale thickener operations have been used to investigate application in solid-liquid separations. The effect of temperature and shear on particle aggregate sizes have been investigated in-situ. Comparison to conventional polyacrylamide based flocculants is favourable. The influence of polymer architecture has been investigated. In continuous operation, the enhanced consolidation of the underflow is limited by the relatively short residence times of the sediment bed within the thickener. It appears the more important benefit of the flocculants may be in the reduced underflow rheology resulting in reduced pumping energy and cost if the polymer cost is not too high. Because the polymers create mineral particles with hydrophobic surfaces, they can be used as flotation reagents. The polymers have been shown to be effective collectors with grade and recovery on par with conventional small molecular weight reagents. The holy grail of improved fines recovery by flocculation/flotation remains elusive.

The Biocide Toolbox: AFM and XPS Studies of Surface Biocides

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The Biocide Toolbox (BTB) is a NZ MBIE funded research programme which has the aim of developing new greener biocide systems with genuine potential for commercialization. The BTB involves about 20 senior researchers and 15 PhD students from four NZ organisations: The University of Auckland (host), The University of Otago, Scion Research Ltd and The Cawthron Institute. This paper is within the theme of surface-presented biocides, one of the four research themes in the BTB. The surface analytical techniques employed are Atomic Force Microscopy (AFM) and angular-dependent X-ray Photoelectron Spectra (XPS). They have been used to investigate mono-molecular and multi-molecular surface layers of the biocide type, siloxane-anchored quaternary ammonium salts (AQAS) (incorporating a C_{18} alkyl chain) on flat quartz surfaces. The AQAS used in this study has been demonstrated to be potent against a wide variety of critical organisms including viruses and several bacteria including the superbug, MRSA. The AQAS is EPA approved and FDA compliant. It should also be noted that AFM has emerged in recent years as a powerful technique for elucidating both bacterial and biomaterials surface processes. Mono- and multi-molecular island films of AQAS (first layer: 2-3nm thick) have been detected using AFM. The angular dependence XPS study of these surface films reveals two N1s signals (c.400eV and c.402eV): the former peak is angular-sensitive so is assigned to the perpendicularly oriented first layer of AQAS.

The authors are grateful to The Ministry of Business Innovation and Employment (MBIE) and Callaghan Innovation for funding the BTB programme.

THE CAPABILITY STRENGTHENING OF INDGENOUS COMMUNITIES THROUGH NATURAL PRODUCTS CHEMISTRY

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In 2004, a partnership was established between the Yaegl Aboriginal community, northern New South Wales, Australia, and the Indigenous Bioresources Research Group on the preservation and development of their customary (traditional and contemporary) plant knowledge so as to improve health and economic outcomes within their community. Comprehensive interviews led to the ethnobotanical documentation of 52 Yaegl foods and medicinal plants. Plant extracts customarily used in the treatment of skin infections and wounds were assessed for their antimicrobial and antioxidant activities, and a number of bioactive natural products have been isolated. Working collaboratively with the Yaegl people has additionally led to community capability strengthening outcomes beyond our initial expectations. For example, in collaboration with Yaegl Elders and bioinformaticians, the web-based Customary Knowledgebase has been built to store both public access and community secure data on customary medicines and foods. Projects have resulted in co-authored scientific publications with the Yaegl community and a medicinal handbook that is used as an education resource. The Yaegl partnership has also led to the highly successful National Indigenous Science Education Program and the cultural immersion program, River of Learning. Similar outputs have been achieved in an international partnership with a tribe in Nagaland, North East India.

Overall a culturally competent and reproducible research framework for working with Indigenous peoples to improve socio-economic outcomes has been built. This presentation will showcase our work and how natural products projects can be used to provide diverse community capability strengthening outcomes.

THE CHEMISTRY OF PYRETHRIN DEGRADATION

Freemont, J,[1] Littler S,[1] Hutt, O,[1] Mauger, S,[1,2] Meyer, A,[1] Winkler, D,[1] Kerr, M,[3] Ryan, J,[1] Cole, H,[3] ***Duggan P***[1,4]

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Pyrethrum, the natural insecticide extracted from dried pyrethrum daisies (*Tanacetum cinerariifolium*) is predominantly composed of six esters, the pyrethrins. These potent insecticidal compounds have the advantage of being rapidly degraded in the environment. The sensitivity of these compounds does, however, present particular challenges in the manufacture and storage of refined pyrethrum extract. A thorough understanding of the chemistry of pyrethrin degradation will help manufacturers to limit losses during crop storage and pyrethrum manufacture.

The photodegradation and mammalian metabolism of pyrethrins was investigated in detail by Casida and co-workers (Casida 1969, 1971). Our presentation will summarise results from the most thorough investigations of pyrethrin degradation chemistry since Casida's seminal work. We have considered a range of chemistries which could be responsible for the degradation of pyrethrins in crop, and during manufacture and storage, and autoxidation has emerged as potentially the most important of these.

The results of the first ever investigation of the autoxidation chemistry of the six isolated pyrethrin esters will be described (Freemont *et al*, 2016). It was found that pyrethrins I and II, the major pyrethrin esters present in pyrethrum, undergo autoxidation more readily than the minor pyrethrin esters, the jasmolins and cinerins. The autoxidation of pyrethrin I and II was found to yield a complex mixture of products, a number of which appeared to also be present in extracts of crop material that had been stored for an extended period. This provided strong evidence that pyrethrin autoxidation occurs in pyrethrum crop on standing.

The Development of Metal-based Imaging and Therapeutics Agents

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The positron-emitting isotope copper-64 is of interest in the development of new diagnostic imaging agents for positron emission tomography (PET). The beta-emitting isotope copper-67 is of interest in designing new radiotherapeutic agents. The two isotopes, $^{64/67}$Cu offer a promising imaging/therapy matched pair for potential theranostic agents. The synthesis and in vivo evaluation of $^{64/67}$CuSarTATE, a copper complex tethered to a peptide that selectively binds somatostatin receptors that are over-expressed in neuroendocrine tumours, will be presented.

Strategies to radiolabel antibodies such as trastuzumab with $^{64/67}$Cu^{2+} will also be presented. Attaching radioactive metal complexes to antibodies or antibody fragments requires careful consideration to avoid compromising the affinity of the antigen-binding site for the target. The use of enzyme-mediated bioconjugation for the site-specific incorporation of a radioactive metal complex into antibodies will be presented.

A final aspect of the talk will discuss new approaches to incorporating positron-emitting zirconium-89 in antibodies and the *in vivo* evaluation of the new constructs in breast cancer models.

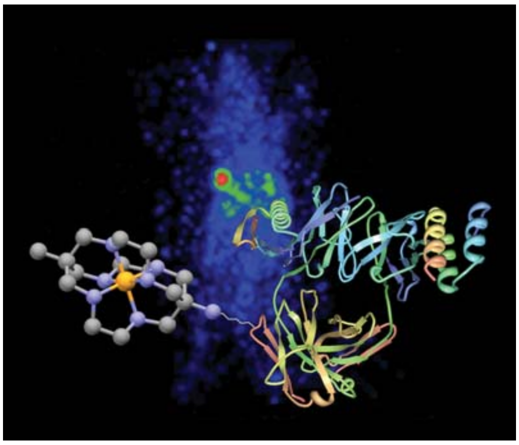

Figure 1. A PET image of a positron-emitting copper complex tethered to the antibody trastuzumab selectively binding to a breast tumour xenograft in a mouse model.

The Development of New Treatments for Multi-Drug Resistant Tuberculosis

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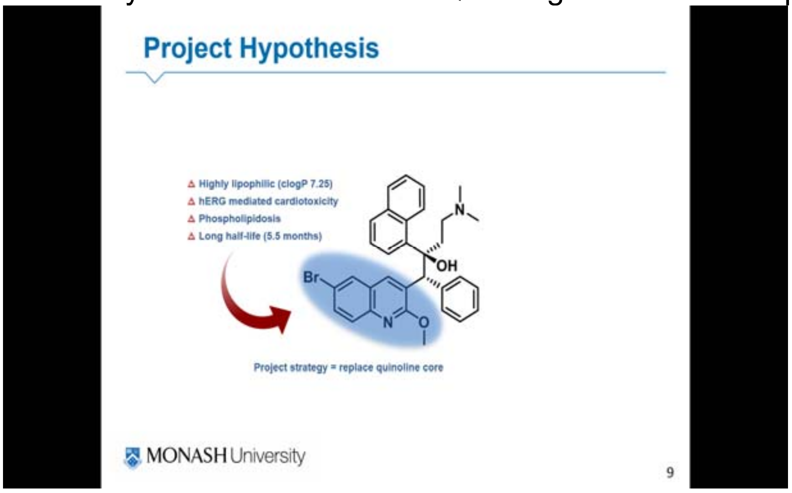
Tuberculosis (TB) is the curable disease that continues to kill, fuelled by the recent increase in multi-drug resistant infections.[1] In response to the urgent need to combat the rise of resistant infections, the novel diarylquinoline drug Bedaquiline (BDQ) received accelerated approval from the FDA in 2012. Despite being highly effective against drug-resistant TB as a result of its unique mode of action (inhibition of mycobacterial ATP-synthase),[2,3] BDQ has been associated with significant toxicities and issues (hERG mediated cardiotoxicity, phospholipidosis, long half-life) and as such, safety concerns are limiting its clinical use.[1]

The key objective of this project was to synthesise novel and distinct analogues of BDQ with modified structural features, designed to retain high potency whilst improving the safety profile and limiting current side effects. To date, a series of analogues have been synthesised and examined for their activity.

This presentation will outline the development of the synthetic pathways utilised to access these analogues, with our initial focus being on the replacement of the quinoline core. The latest results on the activity of these modified BDQ analogues will also be presented.



Project Hypothesis

- △ Highly lipophilic (clogP 7.25)
- △ hERG mediated cardiotoxicity
- △ Phospholipidosis
- △ Long half-life (5.5 months)

Project strategy = replace quinoline core

MONASH University

9

[1] World Health Organisation, *Companion Handbook to the WHO Guidelines for the Programmatic Management of Drug-Resistant Tuberculosis*, Geneva, Swizerland, **2014**.

[2] K. Andries, P. Verhasselt, J. Guillemont, H. W. H. Göhlmann, J. M. Neefs, H. Winkler, J. Van Gestel, P. Timmerman, M. Zhu, E. Lee, et al., *Science* **2005**, *307*, 223–7.

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THE DISCOVERY OF A NEW RADIOFLUORINATION METHOD USING RHENIUM COMPLEXES

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ABSTRACT TEXT

A novel approach to designing positron emission tomography (PET) and optically emitting hybrid medicines was sought, encompassing the chelation of a heterocyclic precursor for fluorine-18 radiolabelling to a phosphorescent rhenium(I) metal centre. The automated radiosynthesis of the multimodal tricarbonyl complex was performed using microfluidic technologies, programed through a computer interface, which allowed for the rapid testing of various reaction conditions. Analysis of these reaction conditions revealed that coordination to the rhenium(I) metal centre enabled nucleophilic aromatic substitution for [^{18}F]fluoride in aqueous-organic solution, which was hitherto unachievable for the non-coordinated ligand. Furthermore, not only did this novel method circumvent the formally required azeotropic distillation of the fluorinating media, though it also significantly improved the radiochemical yield (RCY) compared to anhydrous reaction conditions (affording RCYs as great as 87%, under temperatures as low as 30°C). Fundamental mechanistic studies, as well as application based developments of this method, are currently taking place in order to expand the scope of available PET-Optical imaging agents, and to improve the RCY of both new and existing PET radiotracers.

THE ELECTRICAL DOUBLE LAYER AND CAPACITANCE OF FEW-LAYER GRAPHENE ELECTRODES

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ABSTRACT TEXT

There is an expectation that graphene-based materials will significantly advance supercapacitor technology because they can have very large surface areas. However, the energy storage capacity of graphene to date is well lower than expected for two reasons: The first is keeping the graphene sheets separated as they want to coalesce and thus significantly reducing the effective surface area. The second is the small capacitance of graphene, especially compared to metals, that extends over several hundred millivolts about the potential of zero charge, which has its origins in a quantum capacitance.

There are a number of theoretical studies now that examine this quantum capacitance and they elude to ways in which we might improve the energy storage capacity in a practical way. But experimentally we are well behind in corroborating many of these studies and better understanding of the electrode-solution interface and structure, and its impact on the measured capacitance.

Theory suggests we can increase graphenes low capacitance by introducing sheet defects and chemical modifiers, such as dopants within the lattice, or molecules covalently attached to the surface. But more recently, theory indicates few-layered graphene electrodes may be better for energy storage compared to single layered graphene sheets because the additional graphene layers provide internal screening of the electric field.

In this presentation, we begin to evaluate the electrical double layer of few-layered graphene surfaces and examine the effects of chemically modifying some surfaces with small organic species using aryldiazonium chemistry.

The entropic effect of disordered linkers in allosteric regulation

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

There are many multi-domain allosteric proteins, for example, kinase enzymes and DNA-binding proteins. When adding effective allosteric ligands, the substrate binding domains will be self-regulated by the allosteric binding domains. Intrinsically disordered regions (often be mentioned as linkers) play an important role in this regulation process. Here, we adopted an "entropic-chain" toy model to quantify the entropic effect of linkers. We performed a coarse-grained molecular dynamics simulation on an artificial "Barnase-Barstar" protein system to obtain the free energy differences among different linkers. In thermodynamic analysis, the entropic effect of a flexible linker could be reproduced in chemical equilibrium methods, and the available concentration range was predicted quantitatively. The free energy difference of linker length was about 5.0 RT for the close-open equilibrium, while linker flexibility contributes about 10.0 RT. Linker flexibility property was more sensitive between flexible linker and rigid linker, and could be estimated qualitatively by simplifier models. Moreover, we provided a strategy for general protein pair to exhibit its allosteric potential with a suitable linker.

The influence of freeze drying on Polonium volatility

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Polonium (Po) volatility is well documented even at low temperatures, although, the physical chemistry and mechanisms behind the volatilisation in environmental samples are not well understood.

Biota samples such as plant materials and animal tissues are routinely analysed for radiological isotopes such as Polonium-210 ($_{210}$Po), known to contribute to radiological doses received by both humans and non-human biota. Preliminary analytical preparation of these samples is via desiccation, for example, via oven drying at low temperature to limit the volatilisation of Po. In our laboratory, routine preparation of organic samples has replaced oven drying methods with freeze drying to improve aspects of analytical performance. During freeze-drying, water molecules incorporated into the sample matrix are removed through the process of sublimation and the removal of bound water molecules through the process of desorption. In these methods, heat is replaced with very low temperatures and high vacuum to achieve drying. This study investigated the potential volatility of $_{210}$Po during freeze drying using two different sample types, these were solutions with known polonium activities and chemical matrices and biota samples comprising traditional Aboriginal food items and Australian wildlife. Preliminary results do not show significant losses of $_{210}$Po from the sample which suggests that $_{210}$Po is not volatile under freeze drying conditions.

The molecular origin of anisotropic emission in organic light-emitting diodes

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Organic light-emitting diodes (OLEDs) are increasingly used in electronic displays and related technologies. A major factor in the efficiency of these devices is the loss of photons to reabsorption within the light-emitting layer. These losses can be minimized by increasing the degree of horizontal alignment of the transition dipole moment vectors (TDVs) associated with the phosphorescent emitter molecules. Non-equilibrium molecular dynamics simulations have been used to model the induction of anisotropy in the TDV orientations within an OLED emission layer formed by vapor deposition. Two emitter species were compared: *fac*-tris(2-phenylpyridyl)iridium ($Ir(ppy)_3$), which experimentally shows isotropic emission, and bis(2-phenylpyridine)(acetylacetonate)iridium(III) ($Ir(ppy)_2(acac)$), which displays increased efficiency due to apparent alignment of the TDV. It is found that during deposition, the molecular axis of both emitters becomes preferentially aligned with the normal to the surface. The simulations suggest that the experimentally observed differences in the efficiency of these systems is due to the fact that the three TDVs of $Ir(ppy)_3$ are nearly orthogonal, canceling the effect of the molecular alignment, whereas the two TDVs of $Ir(ppy)_2(acac)$ both preferentially lie parallel to the surface.

THE REACTIVITIES OF DOPAMINE (DA) AND 3,4-DIHYDROXY-PHENYLALANINE (DOPA) DERIVATIVES IN OXIDATIVE NUCLEOPHILIC ADDITION REACTIONS AND APPLICATIONS IN FUNCTIONALISED MATERIALS

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ABSTRACT TEXT

Among the most widely studied biomimetic materials are the materials derived from dopamine (DA), a natural occurring catecholamine. The many applications of polydopamine are a source of continual amazement and have recently been reviewed. Other related natural occurring catecholamines are dehydro DA and L-3,4-dihydroxy-phenylalanine (L-DOPA), the former is implicated in cuticular hardening in invertebrates while the latter is present in mussel proteins. These are not as well exploited for applications in biomimetic materials. Thus although DA, dehydro DA and DOPA are all catechols, the ease of oxidation to quinones and the subsequent nucleophilic trapping that can eventually lead to polymers are likely to be different, suggesting that materials with different properties and functions can be obtained. In this presentation, we report our efforts directed towards the understanding of the reactivities of dopamine and DOPA derivatives as compared to the parent compounds. Specifically we will examine the ease of oxidation of these catechols to the quinones and their reactivities and selectivities of the quinones formed towards nucleophiles. Some examples of the use of these catecholamines in the synthesis of functionalised materials are also described.

THE ROLE OF CHEMISTRY IN ASSESSING WATER AND SEDIMENT QUALITY

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The many thousands of anthropogenic chemicals that reach our natural water systems pose a challenge for regulatory agencies, to determine which of these represent threats to both ecosystem and human health. In Australia and New Zealand, water and sediment quality guidelines are currently undergoing revision, however, we still only have guideline values for less than 100 chemicals. The recommended assessment approach is to use multiple lines of evidence, comprising chemistry, ecotoxicology, biodiversity and bioaccumulation, in a weight of evidence approach, applied separately to both waters and sediments. Chemical assessments involve quantifying potentially bioavailable concentrations of contaminants, often at microgram per litre concentrations and below.

Contaminants of potential concern comprise metal(loid)s, organometals, nutrients, ammonia, and a range of organic chemicals including pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins, pharmaceuticals and personal care products, endocrine-disrupting chemicals, phthalates, and poly-fluoroalkyl substances. Their origins are both point-source and diffuse that include mining and coal and gas industries, agriculture, wastewater treatment and stormwater runoff.

The challenge is to sample and, if necessary, pre-concentrate these compounds from waters and sediments without losses or contamination. For this purpose, a range of passive samplers are available for both metals and hydrophobic organic chemicals, for sampling both surface waters and sediment pore waters. Methods for sampling and analysing a bioavailable fraction will be discussed.

Chemistry also underpins other lines of evidence, providing data on contaminant bioaccumulation and potential toxicity to biota, and, where required, identifying contaminant classes causing toxicity, using chemical separations.

The role of exciton coupling in MCD of light-harvesting complexes

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Photosynthetic light harvesting complexes (LHCs) are very effective in both absorbing light but also, via excitonic interactions between the pigments, transferring this absorbed energy to reaction centres. In reaction centres, the important process of charge separation and subsequent photochemistry takes place. The pigments in LHCs are not usually chemically bonded, but are frequently excitonically coupled.

The strong circular dichroism (CD) of LHCs arises from *intermolecular* angular momentum terms owing to exciton coupling. We have long seen that the magnetic CD (MCD) Faraday *B* term of Q_y transitions of chlorophylls in photosynthetic proteins is often dramatically reduced compared to that seen for an isolated pigment. This is unexpected, as MCD is inherently a property of excitations at a single centre and the effect of two centre terms has shown to be minimal. To date, no satisfactory theoretical basis for this MCD ‘deficit’ has been proposed.

We present MCD data taken of LH2 isolated from purple bacteria. In the analysis, we show the reduction in MCD intensity seen in excitonically-coupled B850 absorption band of LH2 can be beautifully explained in terms differences in coupling within the Q_x and Q_y transitions and the subsequent process of exciton localisation. This analysis is likely to be widely applicable to other LHCs, reaction centres and pigment aggregates in general.

The Stability and Negative Thermal Expansion of Ice VI/2

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ABSTRACT

Being the most important solvent for chemical reactions in environment and living cell, a deep understanding of water properties is of paramount importance. Regardless of its simple molecular structure, water does not share many properties with other liquids. Amongst those anomalous properties are the negative thermal expansivity, as observed both in its liquid and solid phase, and the rich crystalline phases. There are at least fifteen different morphologies of ice in its pure state, and this number increases with the presence of guest molecules that enhance the mechanical and thermodynamical stability of water molecule network. For example, the metastable ice Ic has been reported to be stable at high pressure, of GPa order, in the presence of hydrogen molecule inside its interstitial space. Here, we report the presence of negative thermal expansion of low-density ice VI/2, i.e. one of the sublattice of ice VI, as opposed to the absence of such properties in the high-density ice VI, using only the evaluation of intermolecular interaction potentials. We further show that ice VI/2 stability at high pressure can be enhanced by the presence of hydrogen molecule inside its cavities. The thermodynamic stability is quantified in term of chemical potential that is approximated using van der Waals-Platteuw theory. The Helmholtz free energy of empty ice is calculated as the sum of potential energy of the quenched structure, the harmonic free energy, and the residual entropy arising from the disordered nature of protons in the studied ice structures.

The Stability Of Alcohol And Tobacco Biomarkers In Sewer Systems

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ABSTRACT TEXT

Alcohol (i.e. ethanol) and tobacco (i.e. nicotine) are the two most frequently used recreational substances in the world. The use of both substances are significantly associated with increased burden of diseases, e.g. lung cancer from tobacco smoke and liver disease from alcohol drinking. Therefore, monitoring the consumption of these two substances would help provide evidence for future policies to reduce the health risks that arise from their consumption.

There are several studies using wastewater analysis to monitor the consumption of alcohol and tobacco in different populations. But the potential degradation of ethanol biomarkers, ethyl sulfate (EtS) and ethyl glucuronide (EtG), and of nicotine biomarkers, cotinine (Cot) and trans-3'-hydroxycotinine (HCot), in sewer systems were not fully assessed. Such degradation could lead to the underestimation of the actual consumption.

In this study, we investigated the stability of EtG, EtS, Cot and HCot under different sewer conditions (rising main or anaerobic condition; gravity sewer or aerobic condition both with biofilms; and wastewater only without biofilms) using laboratory-scale sewer reactors. The results showed that:

1. EtG is completely unstable and is not suitable to be used as biomarker to estimate alcohol consumption. Meanwhile, EtS degraded to a lesser extent (average half-life of 2h) but its degradation in a sewer system need to be accounted for in order to improve the accuracy of alcohol consumption estimates.
2. Cot and HCot, are considered stable but Cot is more stable than HCot. Therefore, Cot could be a better biomarker for nicotine consumption in wastewater than HCot.

One Ring To Rule Them All: The synthesis of biologically relevant compounds from cyclopropanes.

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ABSTRACT

The rich chemical diversity of natural products and their often useful biological activity has provided a wealth of structures that lend themselves to the discovery of potential medicines. In fact, nearly 50% of all clinically used drugs are natural products or directly derived therefrom.[1]

Our research program is focussed on the development of new synthetic methods and their application to the synthesis of medicinally relevant scaffolds including natural and non-natural compounds.

Recently we described a method to generate highly functionalised oxazinones from various in situ generated N-acyl cyclopropyl iminium ions.[2] This seminar will discuss our efforts to extend this chemistry to provide robust and rapid entry into highly functionalised chromones. Furthermore, our efforts to apply this chemistry to a series of natural products including bromophycoic acid E, which possesses significant activity against vancomycin resistant enterococcus faecium, will be detailed.

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The Workman–Reynolds “Freezing Potential”: The inherent Physical Process

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

Recently published results and a re-analysis of existing measurements of the Workman–Reynolds Freezing Potential allow a redefinition the electric potential created when ice grows into a dilute salt solution. Since 1948 scientists have measured the freezing potential as ice is grown into dilute salt solutions. Our work published in 2008 and 2010 reported on this voltage as a function of ice crystal face and of salt concentration. That work also produced results based on a variety of freeze rates and discussed some aspects of what is happening at a molecular level at the ice/water interface. Others recently repeated some of our measurements, further confirming the effect, and showing similar trends in the function the voltage follows with time to those found by us in 2010. This similarity has invited this reanalysis. We further elucidated the mechanism by which charges (which are being differentially excluded by the ice interface) are being neutralized over time. In all cases, the measured voltage first peaks after a certain time, and subsequently begins to drop towards zero despite constant growth of the ice. This mechanism of neutralization of the charge build-up we can now state to be unrelated to salt concentration, crystal face, overall ice surface area and, perhaps surprisingly, unrelated to ice growth rate. This new look at the Workman–Reynolds effect shows that the voltage itself is of secondary interest, and rather it is the time to reach peak voltage, which is of paramount interest in the study of the mechanism.

THERMOMECHANICAL PROPERTIES OF BULK HERTEROJUNCTION BLENDS IN POLYMER SOLAR CELLS

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ABSTRACT TEXT

Organic photovoltaics (OPVs) offer a number of advantages, such as fully solid state, compatible with high speed printing and production technologies, but they also a number of challenges related to efficiency and lifetime, many of which can be traced to instability in interfacial layers within the structure.

The structure of the bulk heterojunction – where an exciton is separated into charges – is absolutely critical to the performance of the device. The ideal bulk heterojunction is a co-continuous morphology with a scale length of the order of 20nm. The morphology that is achieved is driven by thermodynamic but limited by kinetics and dependent on the chemical properties and molecular weight of both materials in the heterojunction.

In this presentation, dynamic thermomechanical analysis (DMA) is used in order to follow the development of phases in a range of bulk heterojunction systems fabricated using a range of conducting polymers. Glass fibre reinforcement is used to enhance the mechanical properties of these thin films to allow them to be studied under a range of annealing conditions. Clear relationships between the molecular structure of the conducting polymer, heterojunction structure and device performance are becoming clear.

THREE GENERATION OF PHOTOVOLTAICS

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ABSTRACT TEXT

In 2003, Nobel Laureate Richard E. Smalley outlined humanity's top ten problems for the next 50 years, and the top one problem is Energy. The Sun is a champion among all energy renewable or nonrenewable energy sources and provides the earth with 174 PW in a year. A solar cell, or photovoltaic cell (PV), is a device that converts sunlight directly into electricity by taking advantage of the photoelectric effect. Among all the renewable energy technologies, photovoltaic technology has been considered as the most promising one.

PV technology development must solve the golden triangle issues: low-cost, high-efficiency, long-term stability, and even the fourth issue: environment-friendly. [5] Up to now, there are three generations of solar cells. The first generation cells-also called conventional or traditional cells-are made of polysilicon and monocrystalline silicon, the commercially predominant PV technology. Second generation cells often are defined as thin film solar cells, including GaAs, CdTe, CIGS cells. The third generation solar cells often described as emerging photovoltaics, most of them are still in the research or development phase.

We think that the current classification of solar cells is not reasonable. We suggest that the first generations should be defined as element (silicon) solar cells, including monocrystalline, multicrystalline, microcrystalline, nanocrystalline, amorphous Si cells; the second generations should be defined as compound solar cells, including CdTe, CIGS, GaAs, CZTSSe cells, etc; the third generations should be hybrid (composite) solar cells, including dye-sensitized cells, perovskite cells, organic cells, quantum dot cells, etc

TOTAL SYNTHESIS OF INDOLE ALKALOIDS

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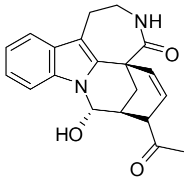
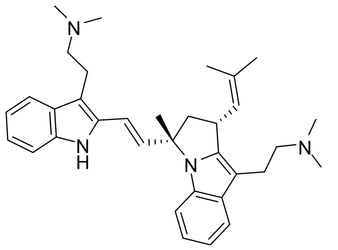
ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

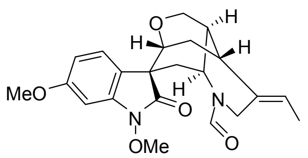
Indole alkaloids have, for many years, provided a fertile proving ground for the application of new strategies and tactics in organic synthesis. In this lecture, our efforts towards a series of never prepared indole targets will be presented. Specific examples include, tronocarpine, the flinderoles, and gelganidine. The underlying synthetic methodologies developed in our lab will also be discussed.



Tronocarpine



Flinderole C



Geleganidine A

Total synthesis of ovafolinin A and B

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Ovafolinin A and B, isolated from *Lyonia ovalifolia* var. elliptica, and *Sinocalamus affinis*, are lignans which contain a unique tetra- and pentacyclic benzoxepin-bridged aryl tetralin structure. We report the first total synthesis of these natural products, in 14 linear steps, utilising firstly an acyl-Claisen rearrangement (**fig. 1**) to racemically construct the lignans, allowing conformation of their unique scaffold and determination of relative stereochemistry. The constrained benzoxepin-bridged aryl tetralin was formed in a single step from a linear precursor via a cascade reaction, using a bulky protecting group to place the reactive moieties in the required orientation.

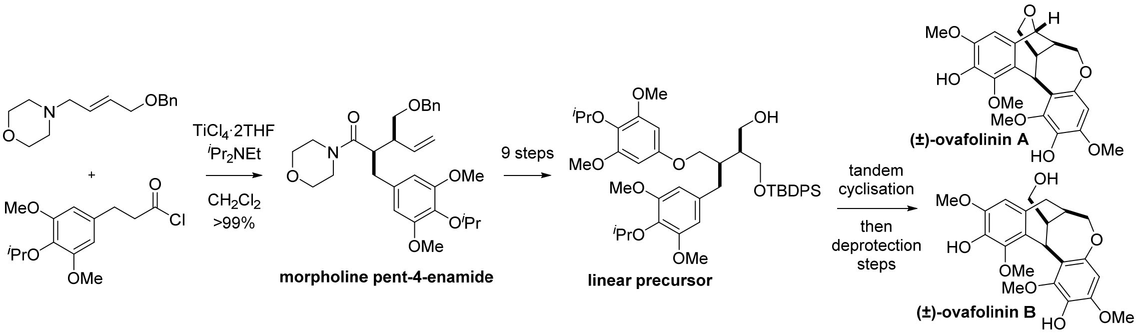

Figure 1: Acyl-Claisen rearrangement to form the disubstituted morpholine pent-4-enamide and subsequent synthetic route to (±)-ovafolinin A and B.

Following confirmation of the relative stereochemistry of both ovafolinin A and B, a slightly modified chiral synthesis was used to confirm the absolute stereochemistry. This chiral route utilised an Evan's chiral oxazolidinone to obtain the same key intermediate, as a single enantiomer (**fig. 2**), resulting in the first synthesis of enantiopure ovafolinin A and B.

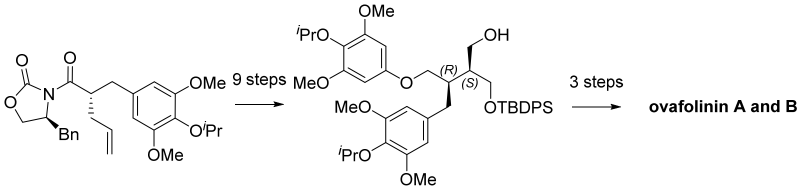

Figure 2: Route to the synthesis of enantiopure ovafolinin A and B.

Total Synthesis of the 5,3’-linked naphthylisoquinoline alkaloids

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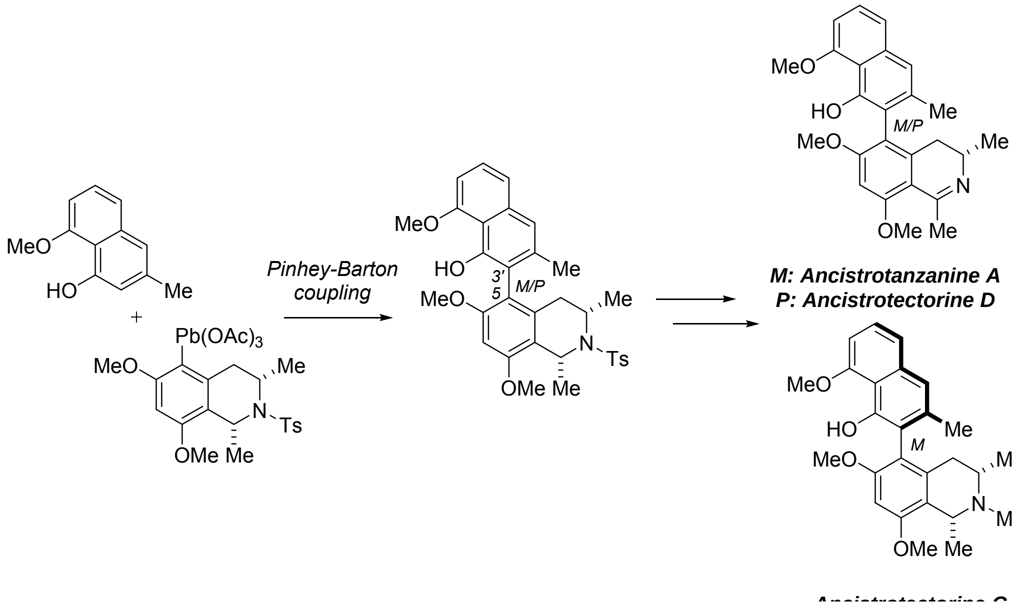
Natural products are an important source of lead compounds for drug development. In the ongoing search for novel treatments against malaria, a promising area of study is the family of natural products known as the naphthylisoquinoline alkaloids, of which over 100 have been isolated to date.

In particular, members of the 7,3’- and 5,3’-linked families not only demonstrate potent antimalarial activity against drug-resistant strains of the virus, but also exhibit low cytotoxicities, making them ideal targets for therapeutic development.[1] However, access to these molecules has been blocked due to the high degree of steric hindrance around the biaryl bond, which presents a significant challenge to their synthesis. To overcome this, previous work in the Morris group has investigated the Pinhey-Barton biaryl coupling reaction,[2,3] successfully applying it in the first total synthesis of a hindered 7,3’-linked naphthylisoquinoline alkaloid, ancistrocladidine.[4,5]

Following on from this work, the first total synthesis of all three 5,3’-linked naphthylisoquinoline alkaloids has now been achieved and will be presented. The synthetic strategy utilises the Pinhey-Barton reaction to generate a common synthetic intermediate from which all three natural products have been prepared.



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Trend in the Agricultural Use of Phosphine

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ABSTRACT TEXT (Arial, 12 font, left aligned, maximum 250 words)

The amount of the preferred grain fumigant, phosphine [PH_3] used to fumigate global grain production would be in excess of 2000 tonne. This gas has many of the properties desirable for a fumigant (e. g. high penetrant ability, low sorption on foodstuffs, very low residue formation). However PH_3 has a major disadvantage: it is flammable and explosive in mixtures with air. The traditional method of generating PH_3 from metallic phosphide formulations is being replaced by high pressure (40 bar) compressed liquefied PH_3 in industrial gas cylinders. While flammability of PH_3 is an issue, the use of pure gas avoids the spontaneous flammability complication associated with pyrophoric trace impurities. The published literature quote the flammability of PH_3 in air to be in the range of 1.8% to 100%. While pure PH_3 does not ignite spontaneously it can when contaminated with impurities such as white phosphorus (P_4) and diphosphine (P_2H_2).

The initial PH_3 product for fumigation of grain was metallic phosphides (e.g. aluminium phosphide, AlP) where the PH_3 was slowly generated over 48 hours from the solid AlP tablet formulation by exposure to atmospheric moisture. The initial gaseous PH_3 formulation in industrial gas cylinders was a non-flammable mixture of 2% PH_3 in CO_2 which allow rapid dispensing of the PH_3 into the grain storage to be fumigated. The more recently the use of 100% PH3 is preferred and can be dispensed by the rapid on-site mixing with air (advantages of lower costs and reduction in the number of industrial gas cylinders required). Application of 100% PH_3 has to overcome the significant acute toxicity and the high flammability issues.

TROPICAL NICKEL HYPERACCUMULATING TREES FROM SABAH, MALAYSIA AND NICKEL BIOPATHWAYS

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The extraordinary level of accumulation of nickel (Ni) in hyperaccumulator plants is a consequence of specific metal sequestering and transport mechanisms, and knowledge of these processes is critical for advancing an understanding of transition element metabolic regulation in these plants. The Ni biopathways were elucidated in three plant species, *Phyllanthus balgooyi*, *Phyllanthus securinegioides* (Phyllanthaceae) and *Rinorea bengalensis* (Violaceae), that occur in Sabah (Malaysia) on the Island of Borneo. This study showed that Ni is mainly concentrated in the phloem in roots and stems (up to 16.9% Ni in phloem sap in *Phyllanthus balgooyi*) in all three species. However, the species differ in their leaves – in *P. balgooyi* the highest Ni concentration is in the phloem, but in *P. securinegioides* and *R. bengalensis* in the epidermis and in the spongy mesophyll (*R. bengalensis)*. The chemical speciation of Ni^{2+} does not substantially differ between the species nor between the plant tissues and transport fluids, and is unambiguously associated with citrate. This study combines ion microbeam (PIXE and RBS) and metabolomics techniques (GC-MS, LC-MS) with synchrotron methods (XAS) to overcome the drawbacks of the individual techniques to quantitatively determine Ni distribution and Ni^{2+} chemical speciation in hyperaccumulator plants.

Tuning Cellular Behaviour Using pH Responsive Nanoparticles.

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The use of nanoparticle delivery systems for biomedicine has generated significant research interest. This is due to the potential of nanoparticle carriers to target diseased cells or tissue and therefore optimise the therapeutic payload to a treatment site. Self-assembled polymeric carriers have generated particular interest for such applications due to their simple and versatile synthesis. However, such carriers are still limited by inefficient delivery to target regions within the cell. Therefore, central to improving the efficacy of such carriers is the need to understand their cellular trafficking. Recently, our research group developed pH responsive nanoparticles that can be used as a model to investigate targeting, internalisation and the endosomal escape of the nanoparticles into the cytosol. Controlling these properties is integral to the design of an effective nanoparticle delivery system. In this presentation, the synthesis of pH responsive poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) nanoparticles will be reported. The ability to control endosomal escape of these materials by tuning the material properties will be demonstrated. Recent work involving the development of protein-polymer hybrids based on PDEAEMA will also be highlighted, including how hybrid nanoparticles can be used to optimise targeting characteristics. The responsive and modular nature of these nanoparticles provides new insights into the design of nanoengineered materials for application in therapeutic delivery.

TUNING POROSITY AND MECHANICAL PROPERTIES WITH CHEMISTRY: HYPERCROSSLINKING POLYHIPES

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Poly(high intrnal phase emulsins)- polyHIPEs are materials prepared by polymerising emulsions with a high volume fraction of the droplet phase (tipically over 75%) with the monomer containing continuous phase (for a review see Pulko I, Krajnc P, Macromol. Rapid Commun. 2012, 33, 1731.). Resulting from an emulsion templating approach are porous polymers with a unique cellular interconnected topology where micrometer sized pores templated by emulsion droplets are connected via interconnecting pores. Pore diameters are therefore normally between a few hundred nanometers and a few ten micrometers. On the other hand, induction of meso and micropores within a polyHIPE is possible with the addition of a porogenic solvent to the monomer containing continuous phase. However, this leads to compromised mechanical properties which is an important issue with polymeric materials of very high porosity. Induction of micropores can on the other hand be performed by post polymerisation chemistry. We have demonstrated that polystyrene based polyHIPEs can be substantially modified in terms of pore size distribution by performing a post polymerisation hypercrosslinking procedure where a radical source is used to initiate further crosslinking of polymer chains which are previously properly solvated. Dynamic mechanical analysis of hypercrosslinked samples showed an improvement in mechanical properties and solvent independent behaviour while gas adsorption experiments revealed a major increase in surface area (from 80 to 380 m^2/g). Another hypercrosslinking approach was performed on a vinylbenzyl chloride based polyHIPEs where applying a Friedel Crafts reaction resulted in an even more dramatic surface area increase (up to 1100 m^2/g).

Two-Dimensional Electrocatalysts for CO_2 Reduction

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Electrochemical reduction of CO_2 using electricity from renewable sources is emerging as a promising approach for reducing global CO_2 emissions and converting CO_2 into useful chemicals. Despite significant progress in the development of electrocatalysts for this reaction, their activities still fall short of the practical requirements of high product yield at low energy consumption and high product selectivity. Two-dimensional (2D) materials have recently triggered tremendous research interest for their unique physical, chemical and electronic properties. They have shown great potential applications in electronics, sensors, energy storage and especially electrocatalysis. Engineering advanced nanocomposites by hybridizing two or more 2D materials or implanting 2D materials on other conductive support to construct 3D electrode are fascinating approaches to overcome the weaknesses of individual counterparts as well as optimise their performance for practical applications. In our recent research, we have developed several 2D nanomaterials, i.e. MoS_2, SnS_2, SnO_2 nanosheets, which are coupled with either reduced graphene oxide or carbon cloth, for electroduction of CO_2 into valuable chemicals, such as CO and formate.[1] The composite catalysts are capable of generating CO or formate at low overpotential and high current density in aqueous medium with good durability. Furthermore, the catalytic mechanism was also investigated by electrochemical and spectroscopic analysis, which will contribute to the design of new catalyst with improved performance.

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TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY AND ITS APPLICATIONS IN METABOLOMICS

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Multi-dimensional chromatography is a system which employs more than one mechanism of separation to a sample, with each mechanism being considered an independent separation dimension. Multi-dimensional gas chromatography is an established technique. However, as with all forms of GC, samples are limited to those compounds that are, or can be made, volatile. In contrast, two-dimensional liquid chromatography (LC×LC) is a relatively new technique and does not require derivatisation. We applied this method to the analysis of mushroom samples and demonstrate that the enhanced resolution and peak capacity allow peaks to be detected that could not be separated using standard, one-dimensional LC.

It has previously been shown that irradiation with UV light increases the vitamin D content of certain mushroom species, but the effect on other nutrients is unknown, and is difficult to assess due to the complexity of the sample matrix. An offline reversed phase x reversed phase LCxLC method was applied to *Agaricus bisporus* mushrooms in order to assess the potential of the technique and the effect of UV irradiation on the mushroom's metabolic profile. The method allowed the detection of 158 peaks in a single analytical run and a total of 51 compounds including sugars, amino acids, organic and fatty acids and phenolic compounds were identified. After irradiation with UV for 30 s the number of peaks detected decreased to 150; 47 compounds increased in concentration while 72 decreased. The data demonstrate that the increased peak capacity of LCxLC has great potential in metabolomics.

ULTRAFAST SPECTROSCOPY OF CHARGE GENERATION IN ORGANIC PHOTOVOLTAIC MATERIALS

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The potential of using organic semiconductor materials as the photoactive component of solar cells has attracted considerable attention over the past decade with photovoltaic efficiencies now exceeding 10%. A major limitation on achieving even higher efficiencies rests on understanding the complex interplay between exciton diffusion, exciton dissociation and charge generation, and the subsequent fate of the charge separated species. The active medium usually consists of a thin film blend of a light absorbing electron donor and electron acceptor and the nanoscale morphology of these intermixed components is recognised to play an important role in the charge generation processes. In order to provide additional insights into the role of blend morphology on solar cell efficiencies, the dynamics of exciton diffusion and charge formation have been studied by ultrafast laser spectroscopy in solid films of new high performance organic photovoltaic materials and in aqueous dispersions of organic semiconductor nanoparticles. For the case of the organic donor-acceptor blend films studied in this work, sub-picosecond transient absorption spectroscopy reveals how fine-scale morphology can be modified to prevent the formation of undesirable triplet states that arise from bimolecular charge recombination, leading to improved photovoltaic efficiencies. On the other hand it is shown that the synthetic method adopted for making aqueous dispersible semiconductor nanoparticles impacts on the nanostructure and the dynamics of exciton transport and charge generation. The results of these studies demonstrate the impact of donor-acceptor blend morphology on the initial photo-processes, and ultimately the efficiency, of organic solar cells.

Undergraduate Chemistry Students' Approaches To Answering Critical Thinking Test Questions.

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ABSTRACT

The development of tertiary students' critical thinking skills is highly desirable as it benefits the individual, the workforce and wider society. As with any learning outcome, aligned assessments must be in place. To this end a pilot Chemistry Critical Thinking Test (CCTT) has being designed and validated. This research describes a validation study conducted with twenty undergraduate chemistry students from a variety of year levels studying at Monash University.

The research with these students enabled the determination of test-retest reliability on the CCTT and convergent validity using a commercially available test. Students were interviewed in focus groups (6-9) to discuss the approaches they took with the various test items. The interviews were transcribed verbatim and qualitatively analysed with a phenomenography theoretical framework to reveal several themes.

The written instructions and examples provided in the introductions of each test allowed students to become familiar with the style of test questions. Students attempted to use the perspective of non-scientists as they had great difficulty restricting personal bias due to their prior chemistry knowledge. Students' carefully evaluated key words and commonly developed rules, hypotheses, diagrams and tables which they used to assist with answering the questions. Finally there was increased awareness of personal assumptions and bias, and evidence the students' critical thinking was being developed through social constructivist learning.

The results suggest a range of approaches in student critical thinking processes and that critical thinking may in fact be developed through engagement with critical thinking tests.

Understanding the Interactions of Natural Organic Matter with Nanomaterials by Capillary Electrophoresis

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Nanomaterials have many applications from drug delivery to food additives.[1] Regardless of their use, nanomaterials eventually enter the environment where they are exposed to Natural Organic Matter (NOM).[2] The NOM adsorbs onto the surface of the nanomaterial changing both their physiochemical properties (such as size, charge and aggregation) and toxicity. The changes from NOM could be both detrimental or beneficial to the nanomaterial's impact to the environment, for example decrease or increase the nanomaterial's toxicity to aquatic organisms.[3] Nanomaterials can exist with many different sizes, shapes, chemical compositions, etc. Thus understanding how the chemical properties of nanomaterials influences their interaction with molecules in the environment, such as NOM, allows for nanomaterials to be designed to have the lowest possible impact on the environment.

Capillary electrophoresis (CE) has been previously used to study the strength of interactions between proteins and nanomaterials.[4, 5] Herein we present a CE method to study the strength of the interaction between nanomaterials and NOM. Through this CE method conditions similar to that of an environmental system can be used providing a representative measurement. The method was developed using silver and gold nanomaterials and was then extended to carbon nanomaterials to determine the influence of a nanomaterial's size and chemical composition on its strength of interaction with NOM.

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Unique Phase Behaviors in Gemini Surfactant/Protic Ionic Liquid Binary Systems: the Role of Hydroxyl Group

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The hydroxyl group in the spacer of a cationic Gemini surfactant (12-3OH-12) or protic ionic liquid (EOAN) caused dramatic phase behavior changes compared to the homologue Gemini molecule or ionic liquid without hydroxyl (12-3-12 or EAN). Here, the effects of the hydroxyl group on micellization and lyotropic liquid crystal formation were investigated through the surface tension, small-angle X-ray scattering, polarized optical microscopy, and rheological measurements. With the hydroxyl group in the spacer, the critical micellization concentration of 12-3OH-12 in EAN was found to be lower than that of 12-3-12 and the 12-3OH-12 molecules packed more densely at the air/EAN interface. At wide concentration and temperature ranges, an interesting coexistence of two separated phases was observed in this 12-3OH-12/ EAN system. Such a micellar phase separation was rarely observed in the ionic surfactant and ionic liquid binary system. With the further increase of surfactant concentration, the reverse hexagonal and bicontinuous cubic phases appeared in sequence, whereas only a reverse hexagonal phase was found in 12-3-12/EAN system. Such unique changes in phase behaviors of 12-3OH-12 were ascribed to their enhanced solvophilic interactions and relatively weak solvophobic interactions in EAN. In EOAN however, only lamellar phase for 12-2-12 and hexagonal phase for 12-s-12 (s = 3, 4, 5, 6) were found. But in all systems, the coexistence of two separated phases could be observed.

We are thankful for the financial supports from the National Natural Science Foundation of China (21373127 and 21673129).

DETERMINATION OF URANIUM AND THORIUM AS WELL AS URANIUM ACTIVITY RATIOS IN SOIL SAMPLES USING ICP-MS AND TIMS

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This paper reports the measurement of uranium and thorium concentration in soil samples using inductively coupled plasma mass spectrometry (ICP-MS) and activity ratio of uranium by thermal ionization mass spectrometry (TIMS). These obtained data can provide very useful information on the source, transport mechanisms and environmental fate of radionuclides. ICP-MS is one of the most powerful techniques for the determination of U and Th. High sensitivity, large dynamic linear range, multi-element capability and possibility to perform isotopic measurements characterize this technique. However any interference or matrix effect arising from ICP-MS analysis can be solved with high resolution, reaction/collision cells and separation. In the present study a methodology has been described for determination of U and Th without involving separation and the method is successfully applied for determination in soil samples from Thailand, Serbia and Japan. Accurate determination of uranium isotope ratio can act as an efficient fingerprint to identify source in case of any nuclear accident. Therefore, analytical chemical separation method has been developed to isolate uranium from environmental sample using Eichrom extraction chromatographic resin, UTEVA prior to TIMS measurement of U isotope ratios.

Use of Carbon Nanomaterials in Solar Cells

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ABSTRACT TEXT

One of the most important issues facing society is the ability to supply the world's energy requirements via both environmentally responsible and sustainable means. Renewable energy, and in particular solar energy, has the potential to address current issues in energy production but costs, both in terms of the energy required for production and final price to the consumer, as well flexibility in terms of system deployment are problems that will need to be addressed. This talk will focus on work using carbon nanomaterials to make new architectures for solar cells. Several possible structures will be explored and the disadvantages and advantages of each will be examined.

Using Probability in Teaching Chemistry

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ABSTRACT

Nature is governed by laws of probability at its most basic level. This concept spans all of natural sciences from biology (theory of evolution; "trial-and-error") to statistical mechanics and quantum theory in physics. We describe case examples of how these fundamental ideas can be employed in the teaching of chemistry: equilibrium states and ionization of amino acids. The fundamental starting point is that chemical concentration is related to the probability of finding particles of reactants/products.

Applying elementary concepts of probability theory - e.g. joint probability AND/OR probability to the probabilistic interpretation of concentration - we can deduce the form of the Law of Mass Action and describe the ionization of ampholytes. All this can be achieved without recourse to sophisticated mathematics. Furthermore, the use of computer algebra software (Maple, Mathematica etc.) allows teachers and students to visualize complex behaviour of molecules with several ionisable functional groups (amino-acids) under different pH conditions. The integration of chemical concepts (concentration), mathematical concepts (probability) and computer visualization is shown to be a powerful tool not only for teaching chemistry but for embedding chemistry in to the wider context of natural sciences. Since chemistry is perhaps the most interdisciplinary of all natural sciences it is important to demonstrate this embedding to students and chemical educators alike.

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Utilizing Long Wavelength Visible Light for Bioorthogonal Polymer Crosslinking Across Tissue

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ABSTRACT TEXT

Light-triggered chemistry has been used extensively in polymer crosslinking for preparation of hydrogels. However, most photo-click reactions rely on the use of UV light which is highly absorbing and damaging to cells and tissue. We report the utilization of red light catalysed oxidation of dihydrogen tetrazine for activation of tetrazine-norbornene inverse electron-demand Diels-Alder conjugation. The activation takes place rapidly under physiological conditions and was applied in polymer conjugation and crosslinking to form hydrogels. Gelation was demonstrated to occur behind a dermal tissue model with a thickness of 1 cm and the crosslinking process is non-toxic to mesenchymal stem cells, enabling encapsulation of hMSC within the gel matrix.

VACUUM RABI CHEMISTRY

Hutchison, J[1,2], Thomas, A[2], George, J[2], Zhong, X[2], Chervy, T[2], Shalabney, A[2], Devaux, E[2], Genet, C[2], Ebbesen, T[2]

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Light-molecule interactions can move into the strong interaction regime when molecules are placed at high density inside nanoscale optical cavities. Under resonant conditions, coherent exchange of photons between the molecules and the cavity generate new, hybrid light-molecule states with consequences not only for chemical catalysis but also energy and electronic transport.

In this contribution I summarize recent progress in the modification of chemical reaction landscapes by strong coupling the zero point energy (vacuum) fields of an optical cavity with collective states of many thousands of organic molecules.

Previously we showed that coupling of electronic transitions of molecules could influence the rate of a photochemical reaction.[1] More recently we have shown that vibrational transitions of molecules can also be strongly coupled with light,[2] leading to changes in the rate of a ground state, thermally-induced deprotection reaction.[3] The latter suggests the ground state Morse potential of the system is reshaped by vibrational strong coupling. The temperature dependence of the reaction rate suggests profound changes also to the nature of the transition state.

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van der Waals forces in nanosystems: new solutions to a sticky problem

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Engineering at the nanoscale is rapidly changing from science fiction to science fact. But, in many nanosystems, the nature of the van der Waals dispersion interactions is weird and difficult to model. We thus report on a novel method[1] for calculating van der Waals forces, which achieves higher accuracy than comparable approaches. Our method is particularly successful in *calculating van der Waals forces in heterostructures* (e.g. MoS_2), in which the low-dimensionality can lead to unusual "many-body" interactions between large numbers of coupled species. Furthermore, these coupled species are often best represented by charged fractional ions – with effective charges far from an integer. Most dispersion methods ignore both many-body and detailed ionic effects. By contrast, our approach *seamlessly includes many-body and fractional charge effects* using a physically justified polarisability model[2] covering Rows 1-6 of the periodic table. Some results of our approach are presented, demonstrating its *ability to outperform comparable approaches* – especially in ionic solids, transition metal dichalcogenides and simplified models of hydrogen storage physics –systems of nanotechnological interest.

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Vibrational spectroscopy: catching hydrogen bonds infra red-handed.

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The importance of hydrogen bonding has long been appreciated, but deeper understanding of its characteristics has led to new definitions of what constitutes a hydrogen bond. Vibrational spectra provide some of the key observable criteria, via perturbations in band position, intensity and width. We have used laser based Resonant-Two-Photon-Ionisation (R2PI) and IR-UV ion depletion spectroscopic techniques to measure the vibrational spectra of clusters selected to display particular X-H···Y hydrogen bonding interactions, and carried out extensive *ab initio* calculations to help analyse and interpret the resultant data. A series of complexes in which a water is bound to molecules with F, Br, Cl or CN groups at the terminus of flexible side chains provides a scale for H-bond acceptors.

Evidence and understanding of sulfur-centred hydrogen bonding, especially where the donor is a thiol, lags far behind that for conventional OH interactions. To help address this deficiency, conformer specific IR spectra of 2-phenylethanethiol (PET) and associated 1:1 solvent complexes have been measured in SH, OH and CH stretch regions. Further calculations on twenty H-bonded clusters with OH/SH donors and N/O/S acceptors demonstrated that thiol SH groups behave like archetypal OH with respect to specific IUPAC proposed criteria for XH···Y hydrogen bond formation.

Visible Light Photocatalysis: Engaging Single Electron Transfer (SET) Processes to Access Novel Heterocyclic Architectures

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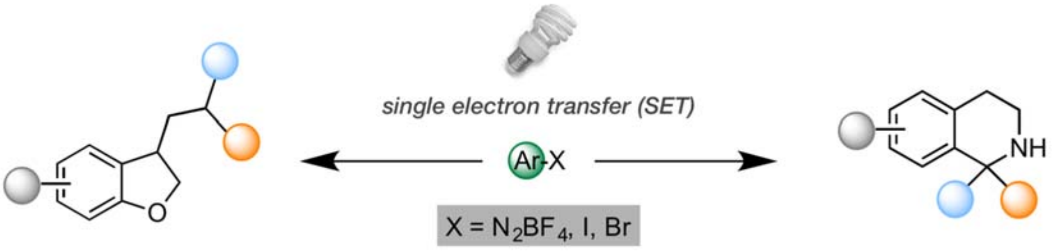
The discovery of new modes of reactivity is fundamental to advances in modern organic chemistry. Visible-light photocatalysis has recently emerged as a powerful synthetic manifold allowing chemists to exploit the vast synthetic potential of single-electron-transfer (SET) processes under mild conditions. The visible light excitation of photocatalysts generates excited state species with strong redox properties, enabling the generation of radical intermediates that can be engaged in the development of new transformations.

Research efforts in our laboratory are driven towards harnessing photocatalysis to furnish novel and diverse heterocyclic architectures through the discovery of SET reaction pathways that operate at ambient conditions. The development of photocatalytic redox reactions that generate fused-ring aza- and oxa-heterocycles with unconventional substitution patterns, and from simple starting materials, will be discussed.



WHAT DON'T I KNOW ABOUT PROCESS SAFETY IN MY FACILITY?

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In today's complex environment we need to manage a range of different aspects of an organisation. Process safety is just one of these aspects, but it can have business ending potential. It is also challenging, as slow degradation or external impacts may not be apparent. The first step is to understand process safety and its often hidden implications. This presentation will explore what process safety is and importantly, what you need to know about it to achieve positive safety outcomes. It will also look at the interaction between process safety and occupational health and safety and how to leverage both for improvement.

X-RAY AND NEUTRON STUDIES OF ELECTRODE STRUCTURE AND OPERATIONAL MECHANISM

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Functional materials form the central part of many important energy technologies, with their atomic-scale structure and chemistry underpinning performance of the whole device. Rechargeable batteries function by moving positively-charged ions between two electrodes that temporarily host them during charge or discharge. The concentration of ions in these electrodes changes over a very large range and the electrode materials accommodate this, usually by either separating into two or more phases, each with a different ion concentration, or by forming a solid solution where the ion concentration changes continuously across a single phase. These different mechanisms of electrode response directly impact how much charge can be delivered (capacity) and how many times this can be done reversibly (cycle life). Generally, two-phase behaviour leads to capacity decay and shorter cycle life, whilst solid-solution behaviour leads to the converse.

Central to advancing rechargeable batteries is gaining an understanding of the electrode phase evolution and structural changes that occur during ion insertion and extraction. Neutron and synchrotron X-ray characterization methods have made important contributions to this understanding, by revealing the details of how the charge-carrying ion is incorporated into and extracted from, as well as moves through, the electrode material. Such information informs the strategic development and chemical engineering of new or modified electrode materials with superior performance characteristics.

In this presentation, examples of where both X-ray and neutron analysis methods, mostly applied in real-time, have been used to understand rechargeable battery electrode function will be given.

(*E*)-2-cyano-3-(4-(diphenylamino)phenyl) Acrylic Acid Extended-Conjugation Derivatives as Sensitizers for DSSCs

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As an efficient electron-donating group, triphenylamine motif is widely adopted in the organic dyes for dye-sensitized solar cells (DSSCs). To investigate the effects on dye property caused by the extended conjugation of electron donating group, three novel organic dyes (FWD1, FWD2 and FWD3) were synthesized by introducing extra phenyl units with different linkers (single bonds, double bonds and triple bonds, respectively) to the phenyl groups of (*E*)-2-cyano-3-(4-(diphenylamino)phenyl) acrylic acid. Starting from 4-(bis(4-iodophenyl)amino)benzaldehyde, single bonds, double bonds and triple bonds can be easily built by the Suzuki Reaction, Heck Reaction and Sonogashira Reaction, respectively. Following the Knoevenagel reaction, the (*E*)-2-cyano-3-(4-(diphenylamino)phenyl) Acrylic Acid Extended-Conjugation Derivatives were synthesized. These three dyes were characterized by ^{1}H NMR, ^{13}C NMR and HRMS, etc. The photophysical and electrochemical properties and photovoltaic parameters of DSSCs sensitized by these three dyes were systematically investigated. The results demonstrate that it is an efficient way to tune the molecular structures by adopting different linkers, which exhibit a significant influence on the dye performance. Furthermore, we can utilize this strategy to develop novel organic dyes for DSSCs.

This work was supported by the Natural Science Foundation of Jiangsu Province (BK20140780).

SYNTHESIS AND APPLICATIONS OF 1-(*Z*)-SUBSTITUTED [3]DENDRALENES

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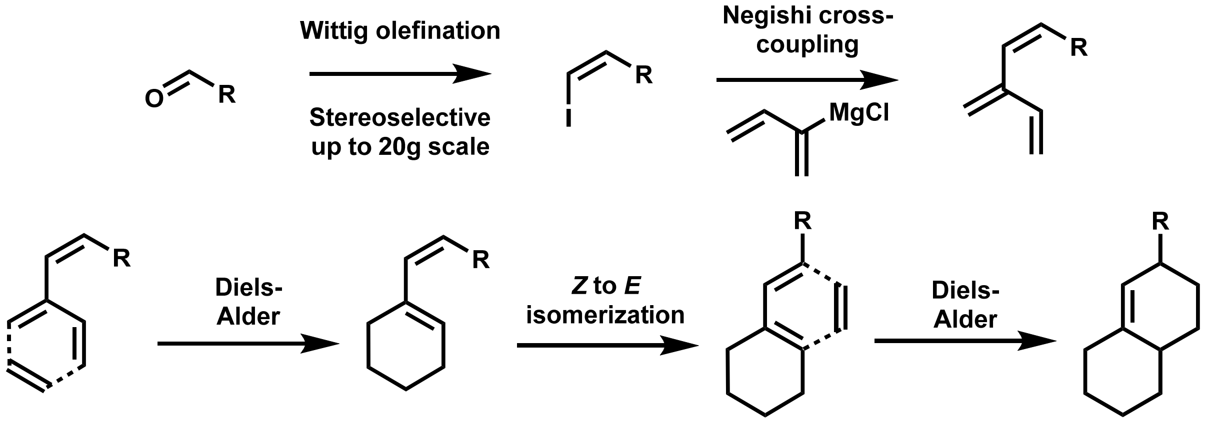
Dendralenes have been under investigation as versatile precursors to complex natural products due to their propensity for diene-transmissive Diels-Alder (DTDA) cyclizations. This synthetic approach is ideal as it maintains high atom economy, has the ability to form many bonds sequentially in a domino-type process, and can be diastereo- and enantioenriched with the use of chiral auxiliaries. Despite these advantages, dendralenes remain underused due to the relative challenges involved in their formation. Synthesis of substituted [3]dendralenes has been accomplished through various methods, though substitution has thus far been mostly narrow in scope[1].

A two-step, highly selective synthesis of (*Z*)-1-substituted [3]dendralenes with broad substrate scope has herein been developed. Stereoselective *Z*-substitution at the 1-position allows exploration of regiocontrol in subsequent DTDA reactions, with the first cyclization taking place exclusively on the non-hindered diene. A second cycloaddition can be performed following facile isomerization of the *Z*-alkene or under high-pressure conditions, with the same or a different dienophile.



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2-(Pyridin-2-ylamino)naphtho[2,3-*b*]furan-4,9-diones as Novel Chemosensors Selectively Binding Hg^{2+} Ion

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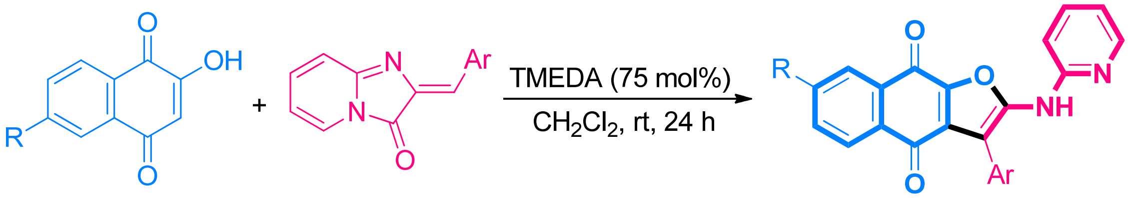
Naphtho[2,3-*b*]furan-4,9-diones are privileged structural motifs of numerous natural products and synthetic analogues.[1] Many of these derivatives exhibit diverse biological activities, including antitumor activity, anti-leukaemic activity, cytotoxic activity toward KB and Vero cells, trypanocidal activity as well as inhibitor of HaCaT cell growth. As a nitrogen heterocycle, the 2-aminopyridine scaffold is also a common structural unit found in a number of synthetic biologically active compounds. In contrast to the interesting applications of naphtho[2,3-*b*]furan-4,9-diones and 2-amniopyridines in the field of drug discovery, naphtho[2,3-*b*]furan-4,9-diones bearing 2-aminopyridine moiety possessing the potential as an important pharmacophore have not been constructed until now. The combination of such parent molecules to form 2-(pyridin-2-ylamino)naphtho[2,3-*b*]furan-4,9-diones systems will not only adds functional diversity but also offers a great opportunity for the therapeutic purposes. In addition, this type of novel naphtho[2,3-*b*]furan-4,9-diones possess rich functional groups, which offers unique possibilities to tune the chemical and/or physical properties and may open up unforeseen opportunities in material science. Herein, we report an efficient and straightforward synthesis of novel naphtho[2,3-*b*]furan-4,9-dione derivatives bearing 2-aminopyridine moiety and their application for recognition of Hg^{2+} ion in aqueous media.



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3D PRINTED MICROMETRE-SCALE POLYMER MOUNTS FOR SINGLE CRYSTAL ANALYSIS

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ABSTRACT

Additive manufacturing, commonly known as 3D printing, has gained considerable recent attention for the preparation of bespoke laboratory equipment at a fraction of the cost of commercial R&D and production. In this presentation I will outline our approach to adapting 3D printing technologies for the preparation of custom integrated loop and pin mounts for single crystal analysis (Figure 1). These crystal mounts were prepared by photopolymerisation of a commercially available resin on a 3D printer purchased for under US$4000. The 3D printing method allowed for rapid prototyping and development of new mount designs, which were prepared at a fraction of the cost of commercially available mounts (excluding the cost of the 3D printer). To our knowledge, these are among the smallest positive features microfabricated by 3D printing for functional laboratory equipment. The suitability of the prepared crystal mounts for X-ray diffraction experiments will be presented, including their applications to the data collection, structure solution and refinement of simple salts, organic and inorganic compounds, and protein crystals.

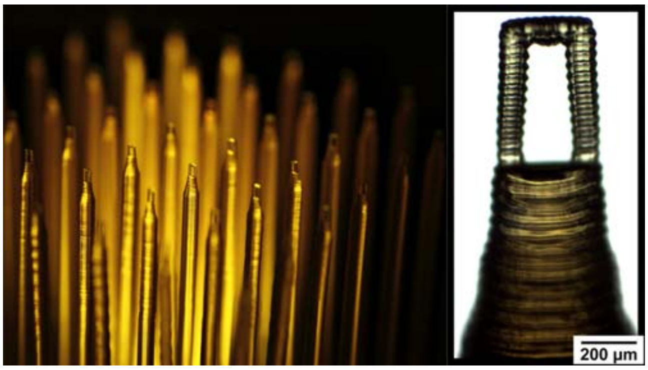

Figure 1: Batch production of 3D printed crystal mounts.

3D Super-Resolution Microscopy of Microtubules in Rabies Cell Models

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Abstract

Super-resolution fluorescence imaging using single molecule localization (SML) has captured images of cell features with resolution in the order of tens of nanometers, well below the diffraction limit of visible light (~200 – 300 nm). Microtubules (MTs) are polymeric protein strands 25 nm wide that form the vital cellular cytoskeleton network that transports proteins throughout the cell and provides structural support, especially during cell division. Their size and importance to cell survival make MTs a common target for super-resolution imaging. MTs have been seen to form large bundles up to 300 nm wide in the presence of rabies virus phosphoprotein 3 (P3)[1]. Recent imaging studies show that specific mutations to P3 reduce its bundling capabilities, revealing that the functionality of P3 *in vivo* correlates with the extent of MT bundling. We have applied astigmatism to SML super-resolution imaging to extract axial information from fluorescent single molecules, revealing their locations in 3D space[2]. Fluorescently-labelled MT strands can be individually resolved down to 20 nm in *xy* and 50 nm in *z*, producing a 3D model that allows visualization of sub-cellular structures with enhanced detail. We will report progress of 3D and dual-colour super-resolution imaging toward quantifying the nature of microtubule bundles induced by viral P3 and other P-protein variants.

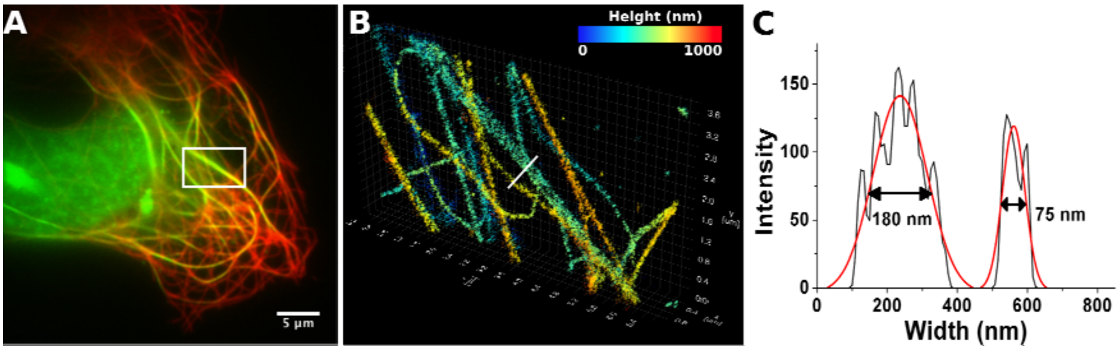

Figure 1. (A) Merged fluorescence image of MTs labelled with Alexa Fluor® 647 (red) and P3 labelled with green fluorescent protein (green) in a P3-transfected COS-7 cell. (B) 3D super-resolution image revealing bundle lies beneath normal MT strands and is much wider. (C) Full-width-half-max analysis of MT bundle and normal MT strand at cross-section in B.

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A CADMIUM-BASED METAL ORGANIC FRAMEWORK STATIONARY PHASE FOR GAS CHROMATOGRAPHY

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ABSTRACT

Metal organic frameworks (MOF) are crystalline porous materials consisting of two main components, metal ions or clusters (cationic part) and organic linkers (anionic part), that combine through coordination bonding to form a well-defined highly ordered framework. Their designable structures along with unique physical and chemical properties such as stability at high temperature and in common solvents, offer new opportunities in separation applications. The adjustable pore sizes of MOF, functional organic backbone structures, and high surface areas are suitable for applications such as selective adsorption as well as size and shape selective separation. Since the first application of MOF for packed column gas chromatography (GC) in 2006, progress in MOF-based stationary phases has been steady over the last decade.

Cadmium-based framework material, Cd(1,4,7,10-tetrakis(4-carboxybenzyl)- 1,4,7,10-tetraazacyclododecane) was synthesised in this study, and incorporated into a capillary column by physical coating of fine particles of MOF onto the inner capillary wall. The GC separation performance of the MOF coated capillary was then evaluated towards target analytes, with investigations focussed on aromatic hydrocarbons. Of particular interest is the relative selectivity of aromatics on the MOF phase, compared with commercially available GC phases. The study demonstrated that there are different retention mechanisms on various columns, observed for the same set of analytes, on MOF compared to commercial stationary phases such as phenyl polymethylsiloxane and polyethyleneglycol. Effects of the temperature program employed, multiple layer MOF coatings, as well as the potential application of MOF in comprehensive two-dimensional GC (GC×GC) will be further investigated and discussed.

TOWARDS THE DEVELOPMENT OF A CHEAP AND RAPID CHEMOSENSING METHOD FOR THE DETECTION OF ALGAL METABOLITES

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ABSTRACT TEXT

In recent years, the global incidence of algal blooms from phytoplankton species in both freshwater and seawater has increased both in frequency and distribution. The threat associated with algal blooms in the marine environment are the phycotoxins that are produced by micro-algae that can accumulate in marine organisms (e.g. shellfish), which are then consumed by humans leading to human toxic syndromes, which could lead to death in some cases. In the context of freshwater, algal blooms caused by cyanobacteria can produce toxins and other metabolites that make freshwater dangerous for drinking and recreation. Some of the cyanobacteria metabolites such as geosmin and 2-methylisoborneol cause objectionable taste and odor in drinking water. Thus during periods of algal blooms, serious problems involving *both* food and water sources can be affected. Although methods already exist for the detection of certain algal metabolites, existing processes are neither very practicable nor efficient as they usually involve extensive processing of samples and the use of expensive instrumentation for detection. In this study, we report the development of a cheap and rapid method for the detection of geosmin (GSM) and 2-methylisoborneol (MIB), based on the principles of chemosensing. Our approach utilized a combination of computational and chemical methods in the design and synthesis of molecular imprinted polymers (MIPs). Through the use of fluorescent tagged compounds, we were able to detect GSM and MIB at the levels of ppb in freshwater.

A flow approach to epoxides and β-amino alcohols

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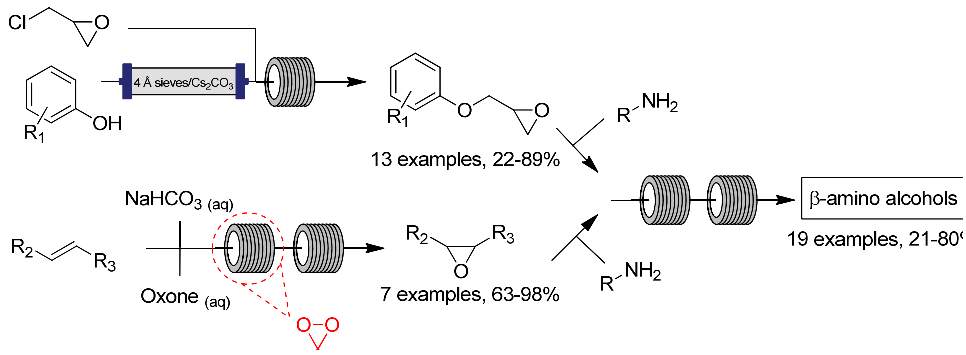
β-amino alcohols are important structural cores in a range of active pharmaceutical ingredients and natural products.[1,2] Traditionally, these compounds have been accessed through aminolysis of epoxides;[3] typically epoxide functionality is installed via either direct coupling of an epihalohydrin, or epoxidation of olefins.[4]

Here we report three chemically robust flow chemistry protocols; (1) epichlorohydrin alkylation, (2) dimethyldioxirane (DMDO) meditated epoxidation and (3) β-amino alcohol synthesis. The investigations commenced with the flow-mediated generation of a range of aryloxy epoxides from substituted phenols using epichlorohydrin. Isolated yields in most cases were good to excellent (56-89%), with one exception (22%). The robustness of this protocol was evident by the generation of ~0.5 g.h^{-1} of desired product.



To expand the range of available epoxides, our investigations next turned to the *in situ* epoxidation capability of DMDO with selected aromatic and aliphatic olefins. This protocol was applicable to a wide variety of starting materials, and the use of the Vapourtec R-series system fitted with autosampler and fraction collector enabled the semi-automated generation of a library of diverse epoxides in moderate to excellent (60-93%) yields. This represents the first use of DMDO production and *in situ* utilisation by flow procedures. Additionally, this protocol demonstrated improved efficiency, ease of purification and safety compared with traditional batch methodologies.[5]

Previous reports of β-amino-alcohols installation using flow chemistry have been limited in substrate scope.[6,7] Here we endeavoured to develop a flow aminolysis protocol which was applicable to medicinal chemistry library development. This methodology is highly robust and showed good regio-selectivity.

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A MICRODIALYSIS-BASED ANALYTICAL SYSTEM FOR DYNAMIC MONITORING OF ARSENIC TRANSFORMATION

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In this study, a microdialysis (MD) technique was combined with high-performance liquid chromatography/inductively coupled plasma mass spectrometry (HPLC-ICP-MS) for continuous monitoring of the dynamic variations of arsenic species in a microbe-inoculated culture broth. After optimizing the analytical system, retrodialysis was applied to assess the probe recovery and analytical performance of the proposed method. The mean probe recoveries of four arsenic species (arsenite, As^{3+}; arsenate, As^{5+}; monomethylarsonic acid, MMA; dimethylarsinic acid, DMA) were in the range from 57.0 to 81.8%. To evaluate the practical applicability of this method, we monitored, continuously for 72 h, the dynamic variations of the concentrations of the four arsenic species in a standardized bacterial sample (ATCC 25922). After adding the arsenic species into the bacteria-inoculated broth, we found that the concentration of As^{3+} decreased over time, whereas As^{5+} increased in concentration. In addition, malondialdehyde (MDA) was also monitored to evaluate the effect of oxidative damage of the arsenic species on the studied microbial system. Our analyses revealed that the dynamic variations of the arsenic species and MDA could be observed continuously during the microbial growth period. This economical and eco-friendly method might also be helpful for monitoring the transformations of other metal species, oxidation processes, and the bioremediation ability of microbial systems.

A New Difluorocarbene Reagent

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A new phosphonium salt, difluoromethylene phosphobetaine ($Ph_3P^+CF_2CO_2^-$), was synthesized. It was found to be a good precursor of difluoromethylene ylide. The difluoromethylenation could be conducted under milder conditions without the addition of external base, giving the difluoroolefinated product in high yield. Moreover, it was found that this difluoromethylene phosphobetaine could be used as the precursor of difluorocarbene. The difluorocyclopropanation or the difluoromethylenation could be performed under milder conditions, which makes the $Ph_3P^+CF_2CO_2^-$ a very good difluorocarbene reagent. In addition, the difluorocarbene derived from this phosphobetaine could be decomposed by DBU and further converted to trifluoromethyl anion without the addition of external fluoride ion. Mechanistic investigation revealed the detailed difluorocarbene conversion process in which the decomposed difluorocarbene was finally transformed into fluoride ion and carbon monoxide. This process was successfully applied in the trifluoromethylation of a variety of (hetero)aromatic iodides, which might turn many difluorocarbene precursors into efficient trifluoromethylation reagents.

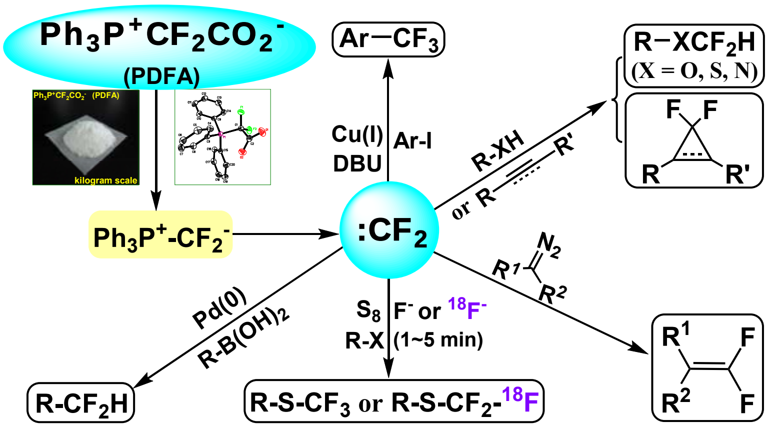

Figure 1: Conversion between carbene, ylide and trifluoromethyl anion.

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A NEW, ONE-POT, MULTICOMPONENT, MICROWAVE-ASSISTED SYNTHESIS OF AZOLO[1,3,5]TRIAZINES

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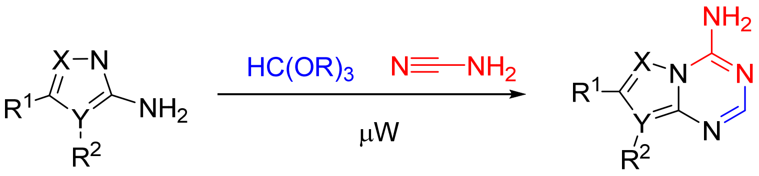
Azolo[1,3,5]triazines are purine isosteres and, due to their resemblance to biological purines, they attracted attention of drug discovery programs. These purine isosteres are actively investigated scaffolds in medicinal chemistry and there is an ongoing demand for the new effective methods for their synthesis. Our attempt to develop a novel multicomponent approach for the efficient synthesis of azolo[1,3,5]triazines stem from the drawbacks of existing stepwise methods. In the optimization stage, a multicomponent reaction of azoles, trialkyl orthoformate and cyanamide under conventional heating resulted in the formation of complex mixtures with low content of the desired product. However, conducting the reaction under microwave irradiation led to a dramatic change in the outcome with improvements in selectivity of reaction, yields and product purity. We further explored scope of our new multicomponent microwave-assisted method and found the aminotriazine annulation onto variously substituted azoles to be successful. The reaction proceeded chemo- and regioselectively affording libraries of azolo[1,3,5]triazines with only slight variations in the optimal conditions for different substituted aminoazoles. The versatility and broad scope of this new microwave-assisted method were proven by our successful synthesis of azolo[1,3,5]triazines. Operational simplicity, short reaction time and high product purity makes this method attractive for the generation of different azolo[1,3,5]triazine libraries in the drug discovery process.



A Novel Catalytic Sensing System for Detecting Formaldehyde

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Artificial enzymes have the catalytic activity similar to those of the natural enzymes. Employing artificial enzymes as the substitutes of the natural enzymes can overcome their intrinsic shortcomings including instability, harsh operating conditions and expensive cost. In recent years, nanomaterial-based artificial enzymes (nanozymes) have attracted considerable attentions due to their high catalytic activity, and facile synthesis.

In this work, it is first time for reporting the oxidase- like activity of β-HgS nanocrystals. β-HgS nanocrystals were found to be able to catalyse traditional enzyme substrates such as 3,3',5,5'-tetramethyl benzidine (TMB) and *O*-phenylenediamine (OPD) to form coloured and fluorescent products, respectively. However, α-HgS nanocrystals did not catalyse these reactions, indicating that α-HgS nanocrystals did not possess the oxidase- like activity. Detailed catalytic mechanism has also been explored. On the basis of the excellent catalytic performance of β-HgS nanocrystals, a catalytic sensing system for detecting formaldehyde has also been successfully developed.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 21377124), the project of new faculty (No. 15BS202), and Promotion Program for Young and Middle-aged Teacher in Science and Technology Research (No. ZQN-YX303) of Huaqiao University.

A Novel Ferrocenyl-based Multichannel Probe For Cu(II) And Hg(II)

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Abstract: Ferrocenyl-based carbazole derivative has been synthesized by a simple one-step reaction and characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS and X-ray analysis. Meanwhile, The newly synthesized receptor **1** displayed reversible fluorescent "turn on" response toward Hg^{2+} with good quantum yield in aqueous environment. The color of the solution containing receptor **1** changed from colorless to yellow upon the addition of Cu^{2+} ions. Therefore, receptor **1** can act as a fluorescent chemosensor for Hg^{2+} and a naked-eye probe for Cu^{2+} in aqueous environment. Quantification of absorption titration analysis shows that the detection limit was 6.15×10^{-7} M for **1**-Cu^{2+} and 6.18×10^{-7} M for **1**-Hg^{2+}, respectively. Finally, the receptor **1** has been used successfully for determination of Hg^{2+} in living cells.

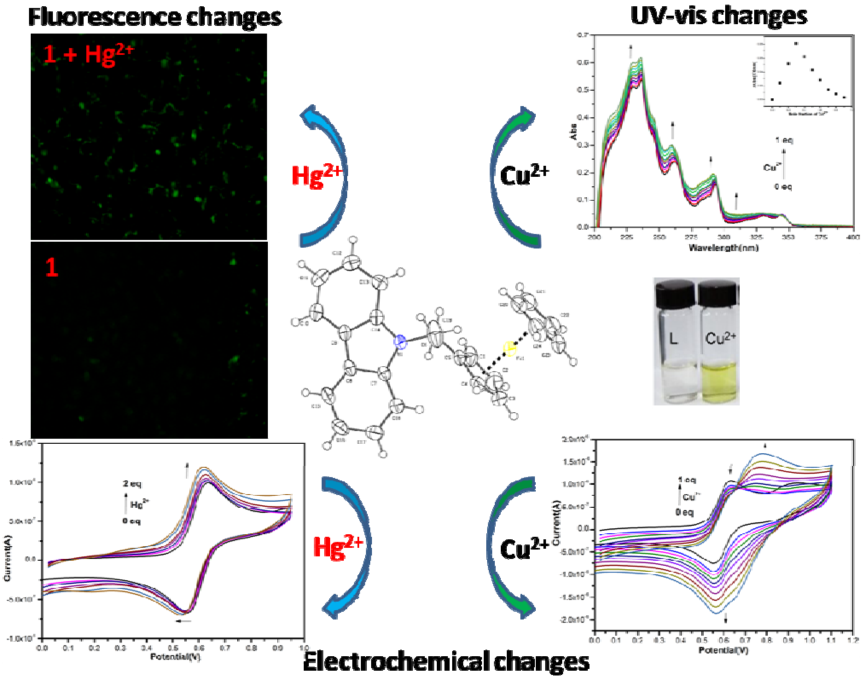

Fig.1.

A NOVEL GRAPHENE OXIDE MODIFIED MONOLITHIC SPE COLUMN

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ABSTRACT TEXT

Through the pre-treatment on the internal surface of the glass syringe and rotating centrifugal effect in the sol-gel process, a monolithic column in the glass syringe has been prepared without gap between the monolithic material and inner-wall of the glass syringe. Additionally, this column can be easily modified by merely flowing graphene oxide (GO) solution through the monolith and then can be directly used as SPE column for quaternary ammonium alkaloids. SEM and elemental analysis indicated GO had been solidly adsorbed on the monolithic matrix and the obtained monolithic SPE column has very good permeability. Compared with the bare monolithic SPE column, the GO modified one shows excellent capability for the extraction of five target analytes (enrichment factor = 40), which is mainly attributed to the electrostatic interactions between the GO and analytes. Duo to the specific properties of GO modified monolithic column, the recoveries maintain high levels when increasing sample loading velocity, which is very different from the packed SPE column. This results in significant reduction of processing time when large sample volumes are involved. With optimal conditions, the GO modified monolithic SPE column was successfully applied in the determination of quaternary ammonium alkaloids in Chinese patent medicine. In conclusion, this method of preparation is highly recommended for preparing monolithic SPE columns with good permeability, high sample loading velocity and great selectivity.

A combination strategy of UV-Visible spectroscopy and chemometrics method applied to simultaneous quantitative-determination on explosive and its byproducts in environmental water:

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2,4,6-trinitrotoluene (TNT) and its byproductsdrinitrotoluene (DNT) pose a significant risk to human health and other living organisms. However, the conventionally analytical methods involved in bulky and expensive instruments are complicated and time-consuming, impeding quick and on-line determination. In the work, a facile yet effective strategy of utilizing UV-Vis spectroscopy coupled with partial least squares (PLS) was proposed, through which TNT and two isomers of DNT in nature water could be rapidly and simultaneously determined without any pre-separation. Variable combination population analysis (VCPA) was utilized to select important feather variables and significantly improves the predictive performance of the PLS model. The calibration set contains 25 samples constructed by orthogonal array design (OAD). The predictive ability of the models was validated by an independent prediction set including 15 samples, achieving up to 0.99 of the determination coefficients (R^2) for each of the analyte. The optimized models were successfully applied to determine the three ingredients in eight environmental samples involving in tap, lake and two kinds of river water with the recovery values close to 100%. Finally, the proposed method is further validated by High Performance Liquid Chromatography, displaying high potential in environmental monitoring.

A Promising Analogue of Gefitinib with Improved Cancer Cell Cytotoxicity

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Gefitinib has been approved for the treatment of advanced non-small cell lung cancer. According to the previous research, the morpholino part of Gefitinib shows no interactions to its anticancer activities due to its weak electron density. In order to modify the electron density of Gefitinib's sidechain, we previously synthesized a series of novel pyrrolidino analogues of Gefitinib that replace the morpholino groups with substituted pyrrolidino groups. We obtained a promising analogue by replacing of morpholino group in Gefitinib with 2-(2-hydroxypropan-2-yl)pyrrolidin-1-yl. We also found that the antitumor activity could be significantly improved by replacing of 3-chloro-4-fluorophenyl group in Gefitinib with 3-ethynylphenyl group. Based on these results, we reported a new Gefitinib analogue FXE-1 with replacing of both morpholino and 3-chloro-4-fluorophenyl groups in Gefitinib with 2-(2-hydroxypropan-2-yl)pyrrolidin-1-yl and 3-ethynylphenyl groups. FXE-1 can be easily synthesized by alkylation with 4-((3-ethynylphenyl)amino)-7-methoxyquinazolin-6-ol and (*R*)-2-(1-(3-chloropropyl)pyrrolidin-2-yl)propan-2-ol. FXE-1 shows higher potent activity against human cancer cell lines, H1975 and SK-OV-3 (human lung adenocarcinoma cell and ovarian adenocarcinoma cell) than Gefitinib. IC_{50} (half-maximal inhibitory concentration) of FXE-1 for H1975 and SK-OV-3 are 2711 nM and 5903 nM, while Gefitinib are 9875 nM and 10000 nM, respectively. It shows that FXE-1 is much more efficient than Gefitinib in term of killing cancer cell, especially for lung cancer cell. The result points that FXE-1 is a promising candidate and it might be an efficient way to develop new drug molecules by combination of efficient motifs in one molecule.

This work was supported by the Natural Science Foundation of Jiangsu Province (BK20140780).

A Quantitative Structure-Activity Model based on Gradient Boosting Decision Tree

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Since an ensemble often has better performance than a single learner, it has achieved successes in many domains. In this paper, A cascaded and ensemble model is proposed to establish the quantitative structure-activity relationship (QSAR) between the overall power conversion efficiency (PCE) and quantum chemical molecular descriptors of all-organic dye sensitizers. The cascaded model is two-level network in which the outputs of the first level, such as Short-Circuit Photocurrent Density (Jsc), Open Circuit Voltage (Voc) and Fill Factor (FF) are the inputs of the second level, and the ultimate end-point is the overall PCE of dye sensitized solar cells (DSSCs). The ensemble method based on Gradient Boosting Decision Tree (GBDT) is adopted in two-level network. The best established cascaded and ensemble model predicts the PCE values of DSSCs with a mean absolute error (MAE) of 0.45, which is about 8.6% of the mean value PCE (5.21%). The validation parameter predictive squared correlation coefficient (Q^2) can achieve 0.83. The results show that the cascaded and ensemble modeling method can effectively improve the computational accuracy of quantum chemical calculation methods, and provides an effective tool for predicting and designing new dye molecules.

A Radical Addition Reaction To Hydrazones “On Water”

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Water is a highly attractive solvent from an economical and environmental point of view because it is cheap, readily available, non-flammable, and non-toxic. Moreover, the unique physicochemical properties associated with water result in the possibility of specific interactions such as polar, hydrophobic, trans-phase, and hydrogen bonding interactions that can significantly influence reactions. However, the major problem associated with the use of water as solvent for organic transformations is its low solubilizing ability towards most organic compounds.

Generally, solvent effect is known to be negligible in radical reactions. Thus, water was employed as medium for radical reactions. In this context, research efforts on radical reactions employing water were towards increasing the solubility of reactants and initiators.

Herein, we wish to report radical addition reactions to C=N bond “on water” at room temperature. In the course of the research, a significant solvent effect was observed. The advantages of this method include high yield, using green solvent, and easy workup. The protocol was applied to the synthesis of isoindolinone derivatives.

A Theoretical Study of P-Heterocyclic Carbenes

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ABSTRACT

The use of N-heterocyclic carbenes (NHCs) as donor ligands is widespread, including application in the stabilizing of highly reactivate elements in the zero oxidation state.[1] Here, we report results from a theoretical study of a number of phosphorus-containing unsaturated five membered ring systems, labelled P-heterocyclic carbenes (PHCs). We have considered analogues of NHCs (with two P atoms), mixed P-N heterocyclic rings,[2] and P analogues of cAAC[3]. We have explored the potential for PHCs to act as analogues of NHCs in stabilising zero-oxidation homonuclear fragments of the form L-E_n-L (L = PHC ligand, E = group 14-15 element, n = 1-2). Our calculations indicate that the L-E_n-L complexes are thermodynamically stable with respect to dissociation. For ring insertion reactions recently observed with NHCs with element hydrides, similar reactivity is not expected for PHCs, although initial adduct formation and hydrogen transfer from the element hydride is thermodynamically favoured. The rate-determining step of ring-expansion is calculated to be too high to be experimentally achievable.

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A Thiophene-containing Polyacetylene Probe for Salicylaldehyde

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A novel polyacetylene containing thiophene (poly(2-ethynylthiophene, PET) was designed and synthesized, and the structure was characterized by IR and NMR. The optical and thermal stability performance of PET was evaluated by TGA, FL, and UV-vis, respectively. The 85% emission of the sensor material was turned off, when salicylaldehyde (Sla) in ethanol was as low as to 0.72 mM. No doubt, the smart performance of the films guarantees that the films may be applied in the chemosensors for aldehydes.

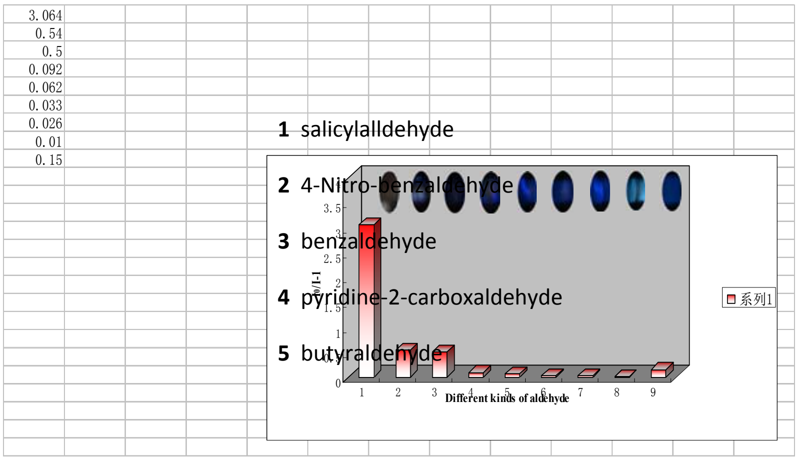

Fig. 1. Emission quenching profile for PET film. The inset shows the photographs of the films in different volatile aldehydes (c=7.0×10^{-5} M).

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ACCESSING *N*-HETEROCYCLES VIA RHODIUM CATALYSIS

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ABSTRACT TEXT

Highly substituted *N*-heterocycles are commonly required for many applications, including medicinal chemistry, however their synthesis can be difficult to achieve. Typically, reactions on a preformed heterocycle can only be achieved at particular sites and reactions require specific substrates which substantially limits the diversity of potential functionality able to be accessed. Recently, the synthesis of various heterocycles has been explored using rhodium catalysts.

Recently it was discovered that rhodium azavinyl carbenes can be readily accessed from *N*-sulfonyl-1,2,3-triazoles. This intermediate is accessed via intercepting the α-diazo imine in the presence of Rh(II). This gives a 1,3-dipole able to undergo a range of intermolecular or intramolecular cycloaddition reactions.

Improving on previously described methodology allowed the synthesis of a highly functionalised fused dihydroindole structure. This fused indole structure has several points of reactivity which can be utilised to further increase the substitution. Of great interest is its ability to act as the diene partner in a Diels Alder reaction to produce a molecule with the ability to probe a greater 3-dimensional space. Interestingly, preliminary results indicate the Diels Alder product is successfully achieved before the molecule undergoes a retro Diels Alder rearrangement to produce a highly functionalised pyrrole.

Acidic-Functionalized Ionic Liquid Catalyzed Cyclization of 2-Sustituted Aminoaromatics with β-Diketones

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ABSTRACT TEXT

Ionic liquids (ILs) are salts being composed of distinct cations and anions that are capable of facilely tuning, and whereby can be designed for task-specific applications through smart choice of the respective cation and/or anion. Based on their unique properties and accomplished capabilities, various ILs have been extensively investigated. [1]

Nitrogen-containing heterocycles have been widely used as important building blocks in pharmaceutical synthesis.[2] Thus, the development of simple and practical methods for construction of these important *N*-heterocycles motifs has stimulated considerable interest. Nowadays, there are several methods to fulfill the construction of *N*-heterocycles. However, toxic metals, strong acids and hash conditions are often unavoidable.[3] Therefore, a milder, environmentally-friendly catalyst system for direct transformation of alcohols still remains to be explored. In our continuing effort on developing ionic liquids catalyzed reactions,[4] herein, we will display our recent progress in cyclization of 2-amino phenol/thiophenols/aniline with *β*-diketones by using acidic-functionalized ionic liquid as metal-free, recyclable, eco-friendly and highly efficient catalysts.

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Adventures in developing introductory laboratory videos for Stage 1 Chemistry

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The first year of study at university is arguably most important for fostering student retention. Research indicates that more than half of students who drop out do so in first year of tertiary study [Starke, 2001]. Research also suggests that first year attrition counts for almost half of all attrition at tertiary level [Willcoxson, 2011]. Therefore, for tertiary educators, ensuring a satisfactory and engaging first year experience is essential!

An important factor in educating stage 1 chemistry students are the practical laboratories. Here we take students who are often unsure and not confident in a laboratory environment and teach them the skills they would need to go on and become successful bench chemists. Part of the experience in the Department of Chemistry at the University of Canterbury is the laboratory talk, a short(ish) introductory talk at the start of each laboratory session to demonstrate the key skills being used in that laboratory. These talks are usually given by our postgraduate cohort, and can vary in quality, and indeed length. They are often less than satisfactory due to sheer logistics; if 40-60 students are trying to see what a laboratory supervisor is doing with a burette or pipette it stands to reason that not all will be able to see or hear clearly.

A group of us set out to remedy this by developing a series of introductory videos for the laboratory experiments. By the time of the RACI congress we should be operating our stage 1 laboratories in a new, purpose built, teaching suite with audio-visual capability, making the development of these resources very timely.

This presentation will outline our experiences thus far in developing these resources, integrating them to our stage 1 teaching programme, with some do's and don'ts along the way!

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Ambient Vapour Pressure Data for Commonly Deployed Lures for Male Fruit Flies (*Tephritidae*: *Dacinae*) by Gas Saturation/TD-GC-MS Analysis

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Dacine fruit fly species are horticultural pests throughout South-East Asia and the Pacific. The Queensland Fruit Fly, *Bactrocera tryoni* (Froggatt), is a major pest in Eastern Australia. Male fruit fly lures, such as cue-lure for *B. tryoni* and methyl eugenol for *B. dorsalis* (Hendel)(Oriental fruit fly), have been used to monitor populations and to control them by methods such as the male annihilation technique (MAT). The effectiveness of these management tools relies strongly on the attractiveness of lures. Metcalf and Metcalf (1992) have shown a linear relationship between lure attractiveness and release rate. The release rate in turn is strongly related to vapour pressure. It is therefore to be expected that lures with a higher vapour pressure should exhibit a higher efficacy. There are, however, no or limited vapour pressure data available for the most commonly deployed attractants. Available data are valid only at elevated temperatures, due to the methods employed (typically the measurement of boiling point over a range of pressures). Estimates of vapour pressures at ambient temperatures require significant extrapolation from such data, leading to large uncertainties. In this study, we describe a gas saturation/thermal desorption-gas chromatography-mass spectrometry (TDGCMS) method for obtaining vapour pressures at ambient temperatures, from 15 °C to 40 °C, and provide vapour pressure data for some of commonly deployed fruit fly lures.

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AN EFFICIENT ONE-POT THREE-COMPONENT SYNTHESIS OF TRIFLUOROMETHYLATED 5*H*-SPIRO[FURAN-2,3'-INDOLIN]-2'-ONES

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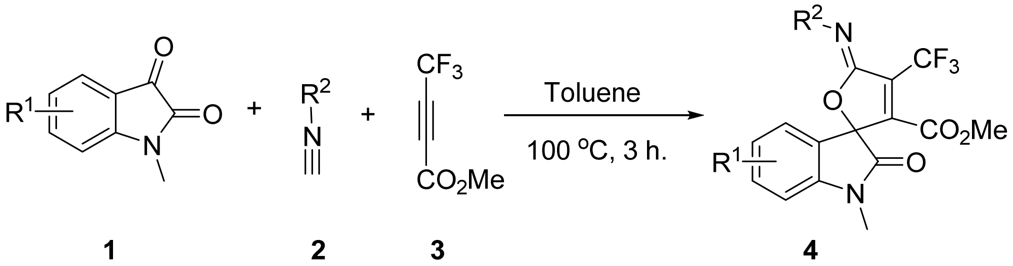
Indolinone is an important class of heterocyclic compounds. The structural units widely present in natural products, drug molecules and functional materials[1]. Numerous studies show that, when introduction of fluorine atom(s) into the heterocyclic compound, it's physical, chemical and physiological properties could be improved significantly[2]. Thus, here we report an efficient method for the synthesis of trifluoromethylated 5*H*-spiro[furan-2,3'-indolin]-2'-one derivatives **4** involving a reaction of *N*-substituted isatins **1**, isocyanides **2** and methyl 1,1,1-trifluorobut-2-ynoate **3** (Scheme 1 and Table 1).



Scheme 1

Table 1 Synthesis of trifluoromethylated 5*H*-spiro[furan-2,3'-indolin]-2'-one **4**[a]

Entry	R¹	R²	Product **4**	Yield (%)[b]
1	H	$(CH_3)_3C$	**4a**	93
2	H	Cyclohexyl	**4b**	82
3	H	Ph	**4c**	89
4	5-Br	$(CH_3)_3C$	**4d**	83
5	5-CH_3	$(CH_3)_3C$	**4e**	90

[a] Reaction condition: **1** (1 mmol), **2** (1.5 mmol) and **3** (1.5 mmol) were stirred in toluene (5 mL) at 100 °C for 3 h. [b] Isolated yields.

ACKNOWLEDGEMENT

We are grateful to the National Natural Science Foundation of China (Grant Nos. 21672138, 21272152, 21542005) for the financial support.

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AN EFFICIENT SYNTHESIS OF PERFLUOROALKYLATED FLUORENES

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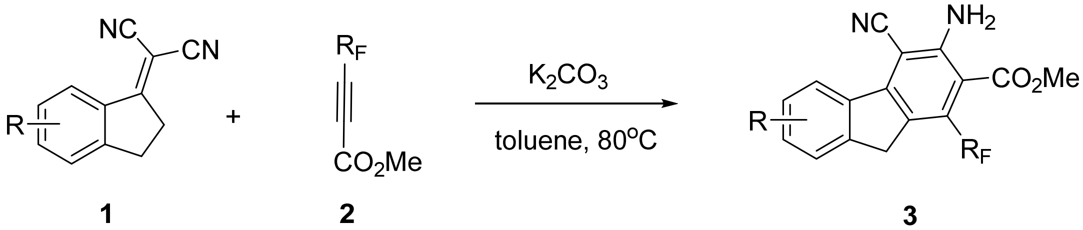
Fluorene is one of the simplest motifs in polycyclic aromatic hydrocarbons, and its derivatives have found broad applications in materials science, pharmaceutical chemistry and organic synthesis[1]. In recent years, the photoelectrical potential of fluorene and related derivatives has become well recognized. Herein we report a novel and efficient metal-free method for the synthesis of perfluoroalkylated fluorene derivatives **3** involving a reaction of 2-(2,3-dihydro-1*H*-inden-1-ylidene)malononitriles[2] **1** and methyl perfluoroalk-2-ynoates **2**. A series of perfluoroalkylated fluorene derivatives **3** were synthesized in moderate to excellent yields (Scheme 1 and Table 1).



Scheme 1

Table 1 Synthesis of perfluoroalkylated fluorene derivatives **3**^{a}

Entry	R	R_F	Product **3**	Yield (%)^b
1	H	CF_3	**3a**	96
2	5-Br	CF_3	**3d**	46
3	H	C_2F_5	**3b**	94
4	5-Br	C_2F_5	**3e**	32
5	H	C_3F_7	**3c**	94

^{a} Reaction condition: **1** (1 mmol), **2** (1.2 mmol), K_2CO_3 (0.1 equiv) were stirred in toluene (5 mL) at 80 °C for 6 h. ^{b} Isolated yields.

ACKNOWLEDGEMENT

We are grateful to the National Natural Science Foundation of China (Grant Nos. 21672138, 21272152, 21542005) for the financial support.

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An electrochemiluminescence sensor for Pb^{2+} based on DNAzyme

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A novel electrochemiluminescence (ECL) sensing platform was developed to detect Pb^{2+} ions based on horseradish peroxidase-mimicking DNAzyme. Poly (diallyldimethylammonium chloride) (PDDA), graphene oxide (GO) and CdS quantum dots (QDs) (Zhang 2015) were used to prepare a composite (P-GO-QDs) which was immobilized on the surface of a glassy carbon electrode (GCE). CdS QDs can produce ECL signal using H_2O_2 as coreactant. The sequence of G-rich DNA strand which named modified T30695 is 5'-NH_3-AAAAAAGGGTGGGTGGGTGGGT-3'. Modified T30695 was attached to P-GO-QDs composite by the reaction between amino group of modified T30695 and carboxyl group of QDs. Modified T30695 can combine with Pb^{2+} to form a stable parallel G-quadruplex (Zhan 2014). The G-quadruplex can further combine with hemin to form DNAzyme which can catalyze the reduction of H_2O_2 and cause the decrease of ECL signal. The signal was measured using a MPI-A analyser, a sensor as working electrode, a platinum wire as counter, and a Ag/AgCl as reference electrodes in 0.1 M phosphate buffer solution (pH 7.4) containing 72 mM H_2O_2. The potential window was from 0 to −1.5 V with a scan rate of 100 mV/s. The ECL signal was linearly dependent on the logarithm of Pb^{2+} concentration from 1.0×10^{-14} to 1.0×10^{-11} M with a detection limit of 9×10^{-15} M. An excellent performance of the ECL sensor indicated that it is promising for Pb^{2+} detection in real samples.

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An Insight About The Role Of Metals In Metallocene Complexes

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ABSTRACT TEXT

Metallocenes like Ferrocene (Fc, Fe(C_5H_5)$_2$) is a perfect example of 'wrong but seminal'(*1*) in chemistry history, resulting constant structure and conformer related frenzied debate due to its strikingly similar properties (e.g. electronic and molecular) and low rotational energy barriers even though its broad application in many fields such as in biomimetic and bioinspired catalyst. The metal related fingerprint vibrations(*2*) were used to establish reaction coordinate method (RCM)(*3*) which proved that the eclipsed is the most stable conformer in both gas and solution phase. Such conformer selective metal related properties and one-on-one correspondence of orbitals both in terms of symmetry and composition lead us to determine a clear insight about the role of metal and ligands in Fc through using excess orbital energy (EOES) tool (*4*). In addition, energy decomposition schemes also indicate the pivotal role of metal in Fc.(*5*) The rotational energy barriers of remaining metallocenes are much lower than Fc itself, making it more challenging to characterize conformers. Therefore, metallocenes with different types of metals such as: alkaline earth metals (such as: Mg, Ca), post-transition metals (such as: Al), and transition metals (Fe, Ni, Mn, Co, and Cr) are used to further understand the differential exclusive role of components (i.e. ligand and metals) of such complexes metals in characterizing closed shell metallocenes conformers through EOES tool(*4*). Additionally, a similar approach is applied for revealing role of metals in different spin orbitals (α and β) of the open shell metallocenes. Preliminary results of the sandwich complexes will be discussed.

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Analysing Multiple Biomarkers for Cancer Diagnosis Based on Logic Gates

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ABSTRACT

Some biomarkers are associated with only one type of cancer, whereas most are associated with two or more cancer types. For example, microRNA-141 shows correlations with nasopharyngeal carcinoma, bladder cancer, colorectal cancers, gastric cancer, pancreatic cancer, osteosarcoma, breast cancer and renal cell carcinoma; carcinoembryonic antigen is a wide-spectrum tumour marker expressed in many types of cancer cells. Besides, there can be opposite correlations between the related biomarkers with the same type of cancer. For instance, in lung cancer, microRNA-21 and epidermal growth factor receptor are overexpressed while microRNA Let-7 and micorRNA-29 are down-regulated. Therefore, a comprehensive and logical understanding of the combinational parameters is in urgent need for the clinical diagnosis and study of cancers. Molecular logic gate and computation provide an ideal solution to untangle the multiple and confused test parameters for a clear conclusion. We proposed a three-target DNA logic circuit, which could be applied for intelligent assay of multiple DNA/RNA targets. In the logic strategy, an "INHIBIT" system can be applied for the simultaneous assay of a positive biomarker and a negative biomarker. We think intelligent assay based on DNA logic gates and DNA computation must be promising and useful.

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Anti-cancer activities of Fe_3O_4-Ce6s-PEG &FAs nanoparticles by photodynamic therapy

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ABSTRACT

Recent progress in nanomedicine has led to the development of magnetic nanoparticles that show great potential for application in early diagnosis, targeted therapy, and personalized medicine. To develop novel multifunctional magnetic nanoparticles (MNPs) with good magnetic properties, biocompatibility, and anticancer activities by photodynamic therapy (PDT), we synthesized multifunctional ferrite nanoparticles (Fe_3O_4-Ce6s-PEG & FAs) functionalized by coating them with chlorin e6 (Ce6) for introducing photo-functionality and by conjugating with folic acid (FA) for targeting cancer cells. The magnetic properties of iron ferrite (Fe_3O_4) nanoparticles in this study have been finely adjusted by controlling the size of the primary Fe_3O_4 nanograins and the secondary superstructed composited particles formed by an aggregation of the nanograins. Singlet oxygen generation from Fe_3O_4-Ce6s-FAs is also confirmed with indirect detection of 1, 3-diphenyl-isobenzofuran photodegradation. Furthermore, we evaluated the activities of the Fe_3O_4-Ce6s- PEG & FAs by checking magnetic resonance imaging (MRI) in vitro, its biocompatibility, and photodynamic anticancer activities on FA receptor (FR)-positive and FR-negative cancer cell lines, Hela, KB, MCF-7, and PC-3 cells, to use for clinical applications. In this study, we have demonstrated that the Fe_3O_4-Ce6s- PEG & FAs have good MRI and biocompatibility with non-cytotoxicity, and remarkable photodynamic anticancer activities at very low concentrations regardless of cell types. These results indicate that Fe_3O_4-Ce6s- PEG & FAs are suitable for effective photodynamic therapy (PDT) and have potential as a therapeutic agent for MRI based PDT, because they have a high value of saturation magnetization and superparamagnetism.

Anticancer activity of Cu(II) and Ni(II) complexes with anthryl thiosemicarbazone

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Inherent and acquired multidrug resistance (MDR) is a huge obstacle to the successful chemotherapeutics of cancer, which is mainly mediated by a P-glycoprotein (P-gp). Much endeavour in overcoming MDR has been made to design and discover novel anticancer agents or P-gp inhibitors, which, up to date, remains still a principal area of anticancer investigation. The anticancer activity of thiosemicarbazones has attracted much attention. In the present work, we found that the chelate compounds $Cu(MNS)_2Cl_2$ and $Ni(MNS-H)_2$ derived from 2-(anthracen-9-ylmethylene)-N-methylhydrazinecarbothioamide showed an improved anticancer activity, with IC_{50} value comparable to that of the clinically used first-line agent cisplatin, while they remained the potential to overcome MDR, which is verified with the standard MTT assay over MCF-7/ADR cells. The drug resistance index (DRI) of MCF-7/ADR cells after treated with $Cu(MNS)_2Cl_2$ and $Ni(MNS-H)_2$ is less than 2, indicating that the chelate complexes could treat an extremely chemoresistant cell MCF-7/ADR as the drug-sensitive one. The cellular uptake experiments suggest that the intracellular concentration of $Cu(MNS)_2Cl_2$ and $Ni(MNS-H)_2$ is almost identical to each other for both MCF-7 and MCF-7/ADR cells, indicating that the function of P-gp is not affect by $Cu(MNS)_2Cl_2$ and $Ni(MNS-H)_2$. Further exploration is needed to reveal the mechanism of $Cu(MNS)_2Cl_2$ and $Ni(MNS-H)_2$ to overcome MDR.

Acknowledgements
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ANTIMICROBIAL AND CYTOTOXIC ACTIVITY OF *COSTUS WOODSONII*

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ABSTRACT TEXT

Costus woodsonii belongs to the Costaceae family. The family is well reported to have diverse pharmacological activities but to-date no scientific study on bioactivity has been reported for *Costus woodsonii*. The aim of this study was therefore to evaluate antimicrobial and cytotoxic activities of methanolic extracts of leaves, rhizomes, stems and inflorescences of C*ostus woodsonii*. Different parts of *Costus woodsonii* were extracted with methanol. Antimicrobial activity was tested using broth microdilution assay against various bacteria strains and evaluated using minimum inhibitory concentration (MICs). The results indicated that the leaves extract showed antimicrobial activities against various *Staphylococcus aureus* strains (MIC: 0.625 mg/mL and 1.25 mg/mL). Apart from that, cytotoxic activity of different extracts was tested against three cancer cell (HT-29, HepG2, H103) and a non-malignant cell (CCD-841) using MTT assay. Rhizome extract exhibited non-selective toxicity against all cell lines. The IC_{50} of rhizome extract was less than 50 µg/mL after 48h treatment for all the tested cell lines. Preliminary phytochemical screening showed that the leaves and rhizomes have tannins, phenols, flavonoids, terpenoids and cardiac glycosides. This study suggests that leaves of *Costus woodsonii* have antimicrobial potential and the rhizomes possess cytotoxic effect, which might be attributed to the bioactive phytochemicals present in the extract.

Antimony containing gunshot residue (GSR) particles from Antimony free primers and their significance in forensic GSR analysis

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In forensic gunshot residue (GSR) analysis, three-component particles containing lead, barium, and antimony, originating from the primer are considered to be the particles most strongly associated with the discharge of a firearm. However, many popular ammunitions on the Australian market, most notably many 0.22 long rifle ammunitions, do not include antimony as a component of the primer, yet still appear to generate three component particles containing antimony (Zeichner et al., 1998), (Lucas et al., 2016). This finding is significant to the interpretation of GSR evidence in firearms crime.

The current research investigates the observation of this phenomena, considering if these are particles retained in the firearm from previous firings (weapon memory effect), or if there is antimony being incorporated into the particles by other means, such as from the surface of the projectile itself. Collection of particles under test firing situations indicates that they are present at a level that suggests retention within the firearm is not the only mechanism at play. Further assessment and analysis of such particles using scanning electron microscopy with energy dispersive x-ray microanalysis (SEM-EDS) mapping indicates that they are indistinguishable from particles obtained from three component primers. Other analytical techniques, including focussed ion beam techniques, have been utilised in order to differentiate particles incorporating antimony from the projectile and antimony from the primer itself.

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APPLICATION OF REDUCED IRON METAL ORGANIC FRAMEWORKS IN CANCER THERAPY

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Cancer encompasses a large number of diseases in which abnormal cells rapidly divide and spread to other parts of the body. In recent years, remarkable strategies have been used to treat the cancer cells selectively. A new and attractive method is generation of free radicals in the cancer environments. Cancer cells exhibit much higher levels of hydrogen peroxide, than normal cells caused during DNA alteration, cell proliferation and apoptosis resistance. Recent studies have shown that different nanoparticles have been used as catalysts for reacting with hydrogen peroxide and produce hydroxyl radical ($OH^•$). The drawback of these studies is that nanoparticles only produced radical at the surface via a heterogeneous reaction, and hence were unable to treat the cancer cells using the endogenous H_2O_2. As a result, exogenous sources are needed to increase H_2O_2 concentration in cancer cells.

In this work, we aim to treat cancer cells by generation of $OH^•$ inside cancer cells without the need for external hydrogen peroxide sources. For this aim, a modified iron metal organic framework was prepared via a hydrothermal method (rMOF). In vitro experiments demonstrate that this novel nanoparticle is significantly more toxic to cancer cells (HeLa) than normal (NIH-3T3) cells. At low concentrations of rMOF, the cancer cell viability decreases dramatically, with no obvious reduction of normal cells (NIH-3T3) cells (Fig. 1A). The calculated half-maximum inhibitory concentration value (IC50) is 60 µg/mL for HeLa cells, which is significantly higher than 113 µg/mL for NIH-3T3 (Fig. 1B).

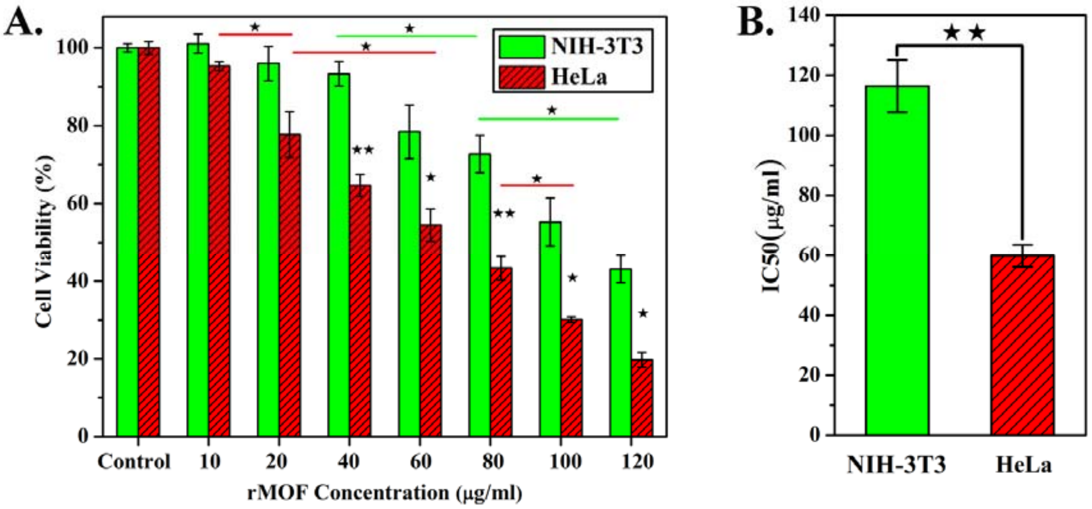

Figure 1: (A) Cytotoxicity of rMOF toward HeLa and NIH-3T3 cells incubated for 24 h. (B) Comparison of the IC50 values of the rMOF in NIH-3T3 cells vs HeLa cells. $^*P<0.05$ and $^{**}P<0.01$.

ARTESUNATE TARGETS THE HUMAN BCL-2 ANTAGONIST OF CELL DEATH PROMOTER

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Artemisinins are sesquiterpene lactones extracted from sweet wormwood (Artemisia annua) and constitute the most potent and safe antimalarials currently available. They also have selective anticancer activity, yet despite their clinical potential, no human target of the artemisinins is known and their mode of action still unclear [1]. In parallel to their antimalarial activity, it is widely believed that the endoperoxide bridge in artemisinins initiates oxidative stress in cancer cells through formation of reactive oxygen species (ROS), which leads to apoptosis [1,2]. Other evidence points to necroptosis or ferroptosis as modes of action.

Starting from artemisinin, we synthesised biotinylated and fluorescently labelled version of artesunate (ART). Biotinylated artesunate was used as bait to interrogate several human cancer cDNA libraries, displayed on the surface of bacteriophage T7. After several rounds of biopanning, we identified a single human target of ART; the Bcl-2 antagonist of cell death promoter (BAD). Fluorescently labelled artesunate was shown to colocalise with BAD antibody in HeLa cells and that the cytotoxicity of ART was abrogated by knocking down BAD with siRNA. We show that ART interacts with BAD in HeLa cells and inhibits the phosphorylation of BAD, thereby promoting the formation of the proapoptotic BAD/Bcl-xL complex and the subsequent intrinsic apoptotic cascade resulting in cell death. This unanticipated role of BAD as a target of ART points to new avenues for clinical exploitation of artemisinins in the Bcl-xL life/death switch.

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ASSESSMENT OF WATER QUALITY OF KARNAFULI ESTUARY OF CHITTAGONG, BANGLADESH.

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The present study was conducted to assess the physicochemical characteristics of water quality parameters and heavy metals concentrations in water at different locations of the Karnafuli Estuary in three seasons during in the hydrological year 2015-2016. Standard methods were followed to determine the physicochemical water quality parameters and heavy metals concentrations. Parameters studied were temperatures, pH, DO, COD, BOD, TDS, EC, total-hardness, alkalinity, chloride and values found in the ranges 25.8-30.1^{0}C, 7.1-8.2, 0.9-7.2 mgL^{-1}, 56-358 mgL^{-1}, 1.3-4.1 mgL^{-1}, 48-975 NTU, 96-1950µscm^{-1} , 20-240 mgL^{-1}, 36.14 mgL^{-1}-130.56 mgL^{-1}, 8-40 mgL^{-1} , 0.21-52.2 mgL^{-1} respectively for water. Concentration of some metals and nutrients such as As , Cd , Co, Cr , Cu , Fe, Pb, Mn, Ni, Zn , NO^{3-} , PO_4^{3-} and SO_4^{2-} , were found in the variation from 0.01-.05 mgL^{-1}, 0.12-0.75 mgL^{-1}, 0.01-.013 mgL^{-1}, 0.051-.063 mgL-1, 0.012-0.25 mgL $^{-1}$, 0.006-4.844 mgL^{-1}, .036-.07 mgL^{-1} , 0.0150.845 mgL^{-1}, 02-.097 mgL^{-1}, .013-0.8 mgL^{-1}, 0.2-6.6 mgL^{-1}, 0.03-3.4 mgL^{-1} , 2.9 -75 mgL^{-1} respectively. The average of maximum parameters studied were found higher than those of the WHO's drinking water guidelines. Data indicates that the water qualities of Karnafuli River are polluted. Halda River , coastal zone and the Bay of Bengal can be affected in this way. Water eco-system pollution is a global concern. This work is an approach through that global goal.

Asymmetric Synthesis of Secondary Borylalkanes through Domino Hydrocupration and Allylation

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ABSTRACT TEXT

A copper-catalyzed multi-component reaction of alkenylborons, allylic phosphates and hydrosilanes has been developed to give the enantioenriched secondary borylalkanes. In the presence of CuC/chiral Walphos catalyst, various alkenylborons furnished the borylalkanes in good yield and with excellent enantioselectivity via hydrocupration and allylation. Alkenyl pinacolboronates and 1,8-diaminonaphthalene borons with an aryl, heteroaryl, or alkyl substituent were well tolerated to provide the correspond products. To demonstrate the utility of this method, a concise synthesis of *(S)*-massoialactone was carried out.

BASELINE PLUTONIUM IN NEW SOUTH WALES AND TASMANIA, AUSTRALIA

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ABSTRACT

Between 1945 and 1980, nuclear weapons injected a range of anthropogenic radionuclides, including several tonnes of plutonium (Pu), into the stratosphere where they were mixed and globally distributed as fallout. These fallout radionuclides are often preserved in soil and sedimentary records. ^{239,240}Pu activity concentrations and $^{240/239}$Pu atom ratios are becoming commonly used in soil and sedimentation studies due to the long radioactive half-lives of these Pu isotopes and enhanced detection techniques.

The inventory of Pu at a given site comprises global fallout and, if present, input from regional and local activities. Australia has a history of nuclear testing in South Australia (Maralinga and Emu Field) and Western Australia (Montebello Islands). Sydney in New South Wales is home to Australia's only nuclear research reactor, and an associated legacy low level waste site where small amounts of Pu and other radionuclides were disposed in the 1960s. To fully understand Pu isotopic measurements at each study site, the local baseline contributed by global fallout must be well-characterised.

This paper establishes the baseline ^{239,240}Pu activity concentrations and $^{240/239}$Pu atom ratios in the Sydney Basin as well as the pristine South West National Park, within the Tasmanian Wilderness World Heritage Area. Presented here is the first history of Pu fallout composition in Tasmania as well as baseline Pu values for the Sydney region. These data provide insight into the variability of ^{239,240}Pu activity concentrations and $^{240/239}$Pu atom ratios and also demonstrate the application of fallout Pu as a chronometer in sedimentation studies and source fingerprinting.

Binding Activated Localisation Microscopy of dsDNA using Molecular Combing

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Binding activated localisation microscopy (BALM)[1,2] has recently been developed as an effective method to obtain super-resolution images of *in vitro* DNA samples. BALM utilises the reversible binding of DNA intercalators, which display increased fluorescence upon binding to nucleic acids, to produce a single molecule concentration of emissive fluorophores within a sample. By cycling the labelling of a DNA structure over the course of an image stack, a high precision image of the original target can be constructed from the accumulation of localisations over time. We have improved the reliability and ease of imaging *in vitro* DNA at a subdiffraction level by combining the existing BALM imaging technique with molecular combing[3]. Molecular combing is able to consistently straighten DNA on poly(methylmethacrylate) (PMMA) coated slides to allow for easy super-resolution imaging. This technique has potential applications in the study of nucleic acid dynamics under different conditions, as well as the behaviour of intercalators and analysis of DNA extracted for cellular samples.

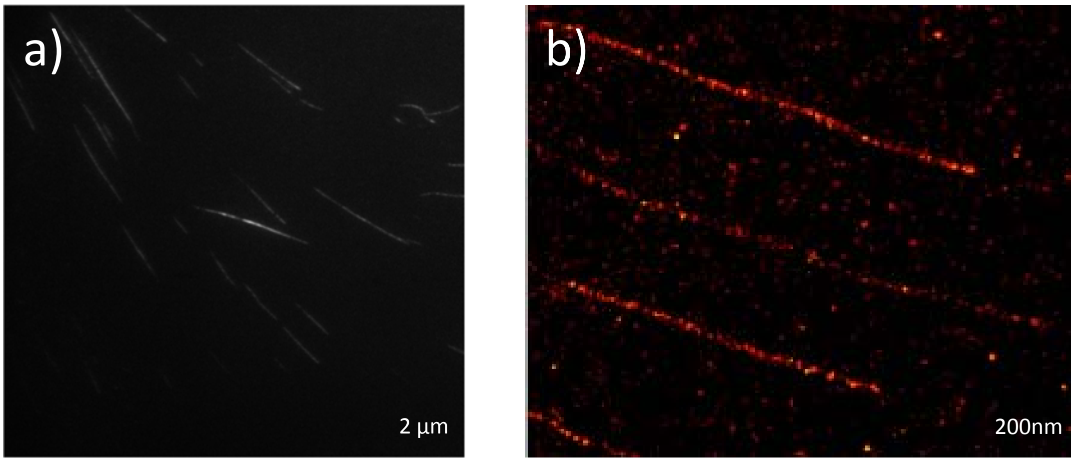

Figure: a) Diffraction limited wide-field image of combed DNA
b) BALM image of combed DNA molecules

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Bioactivity investigation of the extracts from porcupine phytobezoars

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Porcupine dates are bezoar stones that are used in Traditional Chinese Medicine (TCM) treatments such as cancer, post-surgical recovery, dengue fever and etc. The medicinal values have not been scientifically investigated/reported due to availability and high pricing. This paper represents the first report on the phytochemical content, antioxidant, anticancer and anti-inflammatory properties of methanolic extracts of three porcupine dates: grassy date (GD), black date (BD) and powdery date (PD). Phenolic compounds of the porcupine dates were extracted with 100% methanol. We compared the differences between respective porcupine dates based on their (1) phytochemicals constituents, (2) antioxidant properties [Total phenolic content (TPC), Free radical scavenging (FRS), Ferric Reducing Power (FRP), Intracellular ROS scavenging assay (DCFH-DA)], and (3) cytotoxic activity on several cancer cell lines. Tannins, flavonoids, cardiac glycoside, and terpenoids were found in all porcupine dates with tannins forming the major portion in BD and PD, which contribute to its high TPC, FRS and FRP. Methanol extracts of BD and PD (200 µg/ml) demonstrated intracellular ROS scavenging activity in AAPH-induced RAW264.7 comparable to that of 1.84 µg/ml of curcumin, significant NO scavenging activity in LPS-stimulated RAW264.7, and selective cytotoxicity against colon cancer cells HT-29 and HCT-116 but not normal colon cell CCD-841-CoN . Tannins rich fractions of both BD and PD showed increased cytotoxic effects towards HT-29 and HCT-116 cells with lower IC_{50} (45-55 µg/ml) as compared to the crude extract (70-100 µg/ml). Overall, BD and PD exhibited promising *in vitro* and *in vivo* antioxidant, anti-inflammation and colon cancer cytotoxicity properties.

Bio-inspired Energy Conversion in Nanofluidics: A Paradigm of Material Evolution

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ABSTRACT TEXT

Well-developed structure-function relationships in living system become inspirations for the design and application of innovative materials to meet the ever-growing welfare of mankind. Recent advances in chemistry, materials science, and nanotechnology elicit considerable interest to construct ion-channel-mimetic nanofluidic systems for energy conversion and storage as effective as the electrogenic cells. Herein, three essential steps of structural and functional development in synthetic nanofluidic systems are highlighted on the viewpoint of material evolution. By adopting various design strategies from different natural inspirations, the nanofluidic devices and materials keep on evolving and gaining more functions. To acquire asymmetric ion transport functions, the solid-state nanopores transform from cylindrical to conical, and further gain versatile responsibilities via chemical modification. Towards large-scale integration and real-world applications, the structure of the nanofluidic systems experiences an evolution from one-dimensional straight channels to two-dimensional layered membrane. The research progress, challenges, and future perspectives in this growing field are discussed.

Biomimetic Synthetic Approach to the Naphterpin and Marinone Natural Products

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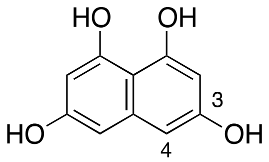
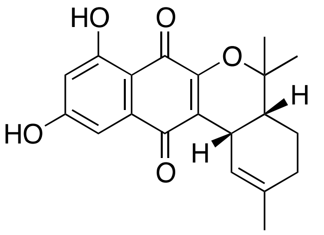
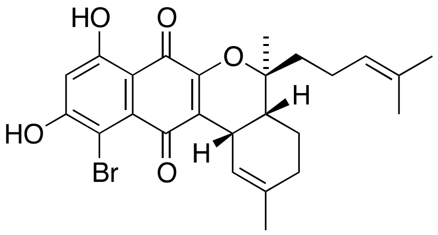
Terrestrial and marine bacteria have long been a compelling source of unique natural products with diverse biological properties and immense potential as therapeutic agents. Naphterpins and marinones are two such families of meroterpenoid natural products with antioxidative and antibacterial properties, isolated form actinobacteria and biosynthetically derived from 1,3,6,8-tetrahydroxynaphthalene (THN). The chemical structure of these natural products is comprised of a polyketide derived naphthoquinone aromatic core and a terpenoid side chain. We investigated a biosynthetically-inspired approach to both the naphterpins and the marinones. This synthesis involves alkylation of the aromatic THN core with a geranyl or farnesyl substituent at the C-4 position, followed by an α-ketol rearrangement to give the desired C-3 substitution pattern of the naphthoquinone. Further key steps include a 6π-electrocyclisation and an intramolecular hetero Diels-Alder reaction. Plausible biosynthetic intermediates will be synthesised and screened against novel enzymes involved in naphterpin and marinone biosynthesis to help elucidate the overall pathway.



THN



7-demethylnaphterpin



marinone

Biomimetic Total Synthesis of (±)-Verrubenzospirolactone

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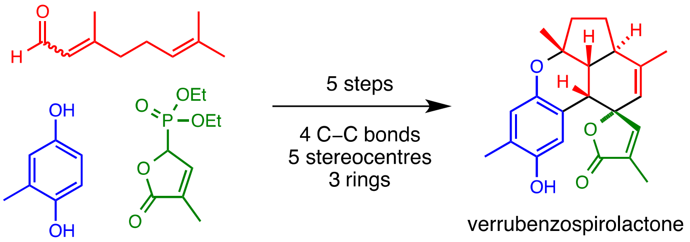
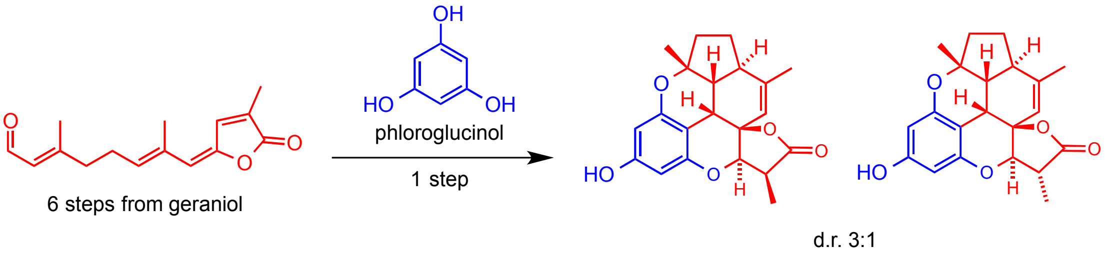
A five-step total synthesis of (±)-verrubenzospirolactone[1] has been achieved using a biomimetic, intramolecular Diels–Alder reaction of a 2*H*-chromene to form two rings and four stereocenters in the final step. This Diels–Alder reaction occurs spontaneously at 30 °C "on-water", and thus suggests that it is likely to be non-enzymatic in nature. The structure of (±)-verrubenzospirolactone was also used to inspire a quadruple cascade reaction to generate seven stereocenters, four rings, three C−C bonds, and two C−O bonds in one step.[2]





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Biopolymer synthesis from 2H-HBO: A renewable chemical

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Synthesis of polymers from the bio-sourced material is of growing interest. Bio-sourced renewable chemicals have the potential to be converted into many value-added products such as biofuels, antioxidants, anticancer drugs, flocculating materials and polymers as well. In this work, we first report the successful synthesis of an acrylic monomer in a greener way and its corresponding polymers from dihydro-5-hydroxy furan-2-one (2H-HBO), which is derived from radiata pine sawdust. This chemical is modified to a new acrylic counterpart which is further homo and copolymerized in different techniques like solution and emulsion. This new monomer is also polymerized by RAFT polymerization to confirm its versatile polymerization capabilities in various conditions. Analytical measurements indicated a thermal stability(glass transition temperature T_g~90°C) and the high molecular weight of obtained polymer from this new green monomer and showed a potential to replace few fossil fuel-based polymers like polystyrene or polymethyl methacrylate.

BIOSYNTHESIS, CHARACTERIZATION, AND ANTIPARKINSON ACTIVITY OF MAGNETITE-INDONESIAN VELVET BEANS (*Mucuna pruriens L.*) NANOPARTICLES

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ABSTRACT

Biosynthesis and characterization of magnetite-Indonesian velvet bean nanoparticle (FeMPn) and its anti-Parkinson pre-clinical test have been conducted. This study consisted of several stages i.e. extraction of velvet bean seed powder, synthesis and characterization of FeMPn and anti-Parkinson pre-clinical test of FeMPn. Velvet bean seed powder was extracted by maceration using ethanol-water (1:1). FeMPn were synthesized from the aqueous solution of velvet bean seeds extract (10,000 ppm) and ferric chloride solution (0.01 M) at 1:1 ratio. The biosynthesised FeMPn were confirmed by SEM, PSA, EDX, FTIR, and TG/DTA. Pre-clinical test was conducted by catalepsy test in mice induced by haloperidol. FeMPn was administered at different doses of 5, 15 and 25 mg/kg body weight. The results showed that FeMPn have a spherical shape with the particle size 50-100 nm. Catalepsy test demonstrated that the three doses of FeMPn can decrease significantly the symptoms of Parkinson's disease such as catalepsy in mice. The optimum dose to decrease catalepsy is 15 mg/kg body weight.

Keywords: Velvet bean, antiparkinson, Mucuna pruriens, nanoparticle, biosynthesis

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Briarenols B–E, New Polyoxygenated Briaranes from the Octocoral *Briareum excavatum*

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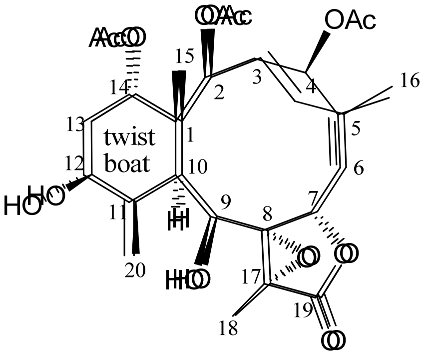
Four new polyoxygenated briarane diterpenoids, briarenols B–E (**1**–**4**), were isolated from the octocoral *Briareum excavatum*. The structures of briaranes **1**–**4** were elucidated by interpretation of spectroscopic data, and the methylenecyclohexane ring in **2** was found to exist in a twisted boat conformation. Briarenols B (**1**) and D (**3**) displayed inhibitory effect on the release of elastase by human neutrophils with an IC_{50} value of 3.33 and 4.65 μM. Briarenol E (**4**) was found to inhibit the protein expression of pro-inflammatory inducible nitric oxide synthase (iNOS) in a murine macrophage- like cell line, RAW264.7, stimulated with lipopolysaccharide (LPS).



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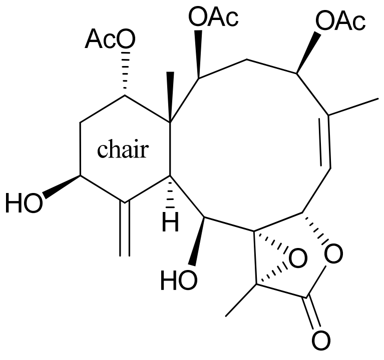

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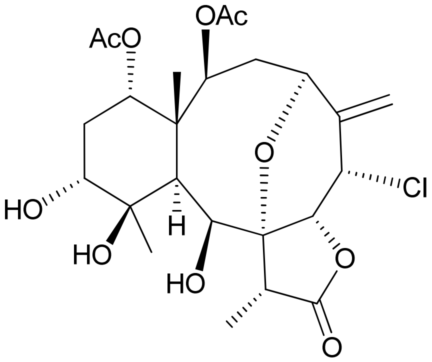

4

Can DFT efficiently model luminescent iridium complexes?

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In the investigation of luminescent metal complexes, possibly the most important property of these compounds are their molecular orbital (MO) energies and HOMO-LUMO gaps. We have been investigating iridium complexes for their use in multicolour sensing applications. Sets of iridium compounds have been investigated in order to explore the potential to tune and alter their electronic properties and subsequently the colour of their absorbance and emission. This has been achieved through the addition of electron withdrawing substituents on the ligands of the complexes which stabilise the HOMO, lowering its energy and increasing the HOMO-LUMO gap.

As part of this investigation, we have explored a variety of DFT methods and their accuracy in the calculation of HOMO-LUMO gaps, as well as solvent and geometry effects in order to identify key differences between these methods. HOMO-LUMO gaps were found to be directly proportional to the amount of Hartree-Fock exchange within the functional, with calculated energies varying from 1.8-10 eV for $[Ru(bpy)_3]^{2+}$.

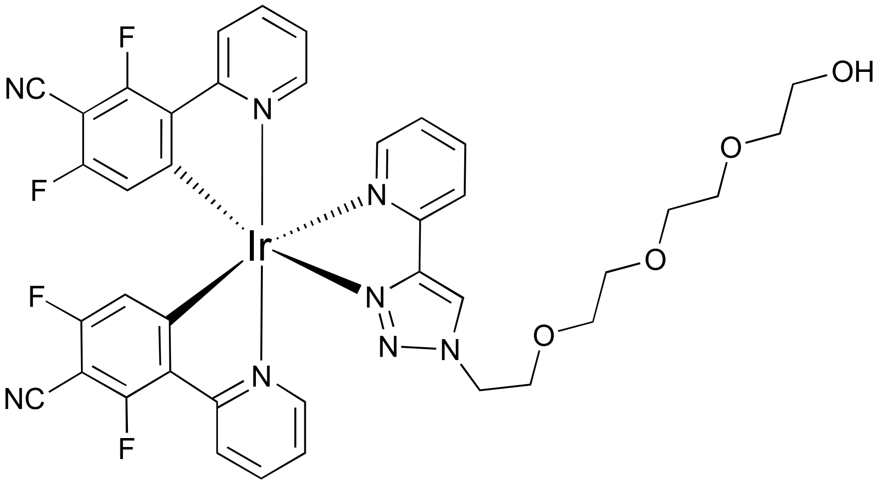

Figure 1: Iridium complex containing PEG group to enhance aqueous solubility.

Can the Toxicity Characteristics Leaching Procedure (TCLP) Test Predict Lead Bioavailability?

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ABSTRACT

Lead contamination in soils is a high profile environmental issue. The association between lead exposure, blood levels in children and their general health and development means that there is a strong community interest in the risks associated with lead-contaminated soils.

Under the risk assessment methodology contained in Australia's *National Environment Protection (Assessment of site contamination) Measure 1999*, lead bioavailability is almost the only variable input to risk assessment calculations. The Physiologically-Based Extraction Test (PBET) is designed to mimic human gut conditions and provide an estimate of lead bioavailability. However, the PBET is not widely used by Australian contaminated sites practitioners, for a variety of reasons. Conversely, the TCLP test is widely used in contaminated sites assessment, and most practitioners are familiar with it. It is generally used to indicate contaminant mobility and leachability.

The author conducted a literature search to identify if studies have been undertaken to establish a correlation between TCLP and PBET. No such studies were apparent, but the data available on lead leachability, bioavailability and remediation allowed a limited statistical analysis to be conducted on the results from the use of both tests on the same materials. The results show that there is not a statistically significant correlation between the results of the two tests. Hence, there should be caution exercised in attempting to use TCLP data in risk assessments for lead contamination.

Detection and Induction of Cell Death of Cancer Cells by Luminescent Iridium Complexes Having Death Receptor Binding Peptides

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TRAIL is a cytokine classified in TNF superfamily that triggers apoptosis in a wide variety of cancer cells by complexation with death receptors (DR4 and DR5).[1] TRAIL is a C_3-symmetric protein consisting of three monomeric units.[1] Cyclometalated iridium (III) complexes such as *fac*-Ir(tpy)$_3$ (tpy = 2-(4-tolyl)pyridine have excellent luminescent properties and possess C_3-symmetric structure like TRAIL.[2] Therefore, Ir complexes having DR binding peptide are expected to detect cancer cells and induce their cell death. Recently, Ir complexes having cationic peptides have been reported to induce Jurkat cells death and exhibit strong emission in dead cells.[3]

In this study, we report on the design and synthesis of luminescent Ir complex-peptide hybrids (IPHs) having DR5 binding peptide.[4] IPHs are capable of binding with DR5 and detecting cancer cells such as Jurkat, K562 and Molt-4 cells. Microscopic images and flow cytometry data suggest that IPHs bind with these cancer cells in a parallel manner to the DR5 expression. Co-staining of Jurkat cells with IPHs and anti-DR5 antibody, disclose that IPH-DR5 complexes internalize into cytoplasm via endocytosis and induce necrotic type cell death of cancer cells possibly via calcium overload. To the best of our knowledge, IPHs are the first class chemical agents that detect cancer cells and induce their cell death.

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Carboberyllation: addition of organoberyllium species to alkenes and alkynes. A comparison with carboboration.

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Carbometallation reactions are widely used and are of great importance in organometallic chemistry, but carbometallation has not been reported for beryllium (carboberyllation). This is significant, as Be is predicted to have the richest organometallic chemistry of any atom in the s-block due to its relatively high electronegativity. However, research into organometallic Be chemistry is suppressed due to the high toxicity of Be containing complexes. This makes predictive computational studies highly valuable in identifying which classes of reactions will be the most feasible in the study of organometallic Be chemistry, thus allowing those synthetic chemists with the skill to handle Be to choose the most promising reactions. Here we demonstrate that barriers for the addition between $BePh_2$ and alkynes are as low as 100 kJ/mol. Our data shows that for both terminal and internal acetylenes a 1,2-regioselectivity of the addition is expected, in contrast to the carboboration reactions.

Carbon Dots/$NiCo_2O_4$ Nanocomposites with Various Morphologies for Hybrid Supercapacitors

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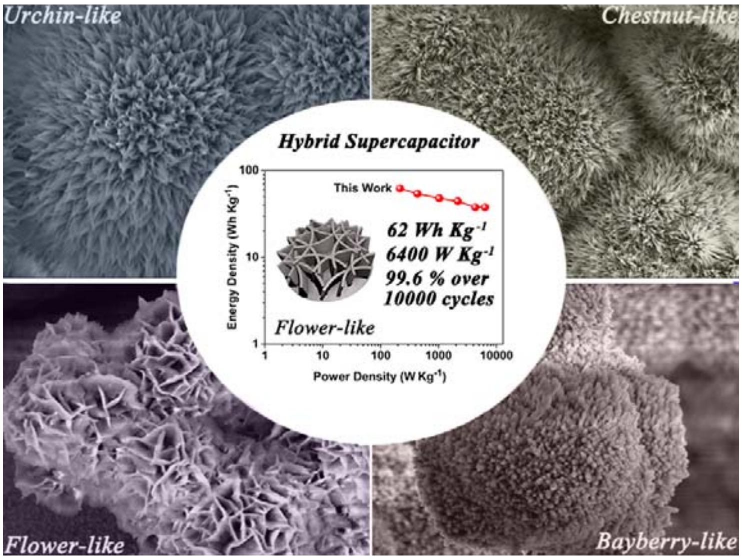
ABSTRACT TEXT

Carbon dots (CDs) have become a focus due to their unique properties in both physics and chemistry. Besides the widely reported fluorescence sensors or bioimaging probes, CDs can also be used as electrode materials in supercapacitors and fuel cells.
For supercapacitors, high power density and excellent coulomb efficiency are their natural advantages. But the typical supercapacitors fail in the lower energy density because their energy storage is limited on the electrode surfaces in form of the double layer capacitance. To overcome this limitation, electrode materials should possess abundant reversible redox reactions to realize high energy density. For example, nickel cobalt oxides ($NiCo_2O_4$) have promising high energy densities which are based on the metal valence variations in redox reactions, while some deficiencies like volume change effects always render the short life cycles and poor rate performances of $NiCo_2O_4$ materials .
To dissolve this problem, we prepared the novel CDs/$NiCo_2O_4$ nanocomposites. By adjusting the inventory rating of CDs in reactions, multi-structures of the composites were achieved from sea urchin to flower and even bayberry. The specific capacitance of the optimal sample reached 2168 F g^{-1} and the retention rate exceeded 75% when the current density varied from 1 to 30 A g^{-1}. A hybrid supercapacitor was fabricated by using CDs/$NiCo_2O_4$ as positive electrode and hierarchical porous carbon as the negative electrode, respectively. Such device exhibited a high energy density of 62 Wh kg^{-1}, and even a 99.9% capacity retention rate after 5000 cycles at a high current density of 30 A g^{-1}.



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Catalysis by Applied External Electric Fields

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Applied external electric fields (EEFs) have been known to be able to accelerate the rate of redox reactions for quite some time and more recently have been shown to also have an effect on the rate of non-redox reactions (Aragonès et al., *Nature* 2016) with both computational and experimental results. Computational studies have also shown that EEFs have the potential to act as switching agents and can create selectivity between reactions where there was none before (Shaik et al., *JACS* 2004) without the need to alter reactions conditions except for the EEF. The potential versatility of using EEFs as rate enhancing agents in many different types of reactions and their potential reaction switching activity, as well as the low cost associated as compared to some of the more traditional catalyst species makes them of great potential impact in both the industry and research fields.

This presentation will explore computational results of EEFs on a range of reactions and explain why EEFs are able to catalyse and alter these reactions as well as suggest further areas of study and potential future applications for this emerging field of chemistry.

CATALYST FREE SYNTHESIS OF DIHYDROPYRANO PYRAZOLE DERIVATIVES USING PEG-400

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The use of greener and safe reaction media in place of volatile solvents have been considered as an essential part of organic synthesis. To address the problems caused by volatile organic solvents, liquid polymers or low melting polymers are developed as an alternate medium for the organic synthesis. In this direction, PEG-400 is emerged as an important reaction media due to their thermal stability, non-toxicity, recyclability and water solubility.

On the other hand, fused pyran derivatives represent promising class of bicyclic heterocycles which constitute structural unit of many therapeutic agents and natural products. Pyrano[2, 3-c]pyrazole derivatives are such compounds gained major attention due to their potent biological activities.

In view of these aspects, a simple and efficient method for the synthesis of dihydropyrano[2, 3-c]pyrazole derivatives has been attempted. A series of dihydropyrano[2, 3-c]pyrazole derivatives are synthesized under catalyst free condition using PEG-400 as reaction medium. All the products were characterized using FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The method uses PEG-400 as green reaction medium which facilitated improved yield in the formation of dihydropyrano [2, 3-c] pyrazole derivatives and was found to be as efficient as that of catalysed reaction.

Catalytic Activity of Pd-Cu Core/shell Nanoparticles for CO Oxidation

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Designing new materials for heterogeneous catalysis is interesting and challenging in surface science. For years, scientists have found out that the bimetallic system can achieve better catalytic performance due to effects such as ligand effect and ensemble effect. Since the reactivity of bimetallic overlayer can be tailored by substrate, the bimetallic nanoparticle with core/shell structure is promising due to its easy way of the formation with the effect of phase separation. In this paper, self-consistent periodic density functional theory (DFT) calculations have been performed to study the catalytic activity of Pd-Cu bimetallic alloy for CO oxidation. The bimetallic alloy consists of fixed three-layer Cu(111) substrate and N-layer pseudomorphic Pd atoms which is denoted by NL-Pd/Cu(111). The adsorption energies and catalytic activities of Pd-Cu bimetallic systems depend largely on the electronic structure of surface Pd atoms near the Fermi level which is affected and modified by substrate Cu. A linear relationship is found between the adsorption energy (E_{ad}) and the d-band center (ε_d). With nudged elastic band (NEB) method, we have calculated the energy barriers for O_2 dissociation and CO oxidation with atomic O. The dissociated atomic O can react with CO via Langmuir-Hinshelwood (LH) mechanism with low energy barriers on proposed Pd-Cu bimetallic surfaces. An opposite trend is observed for O_2 dissociation and CO oxidation energy barriers with respect to d-band center. We have mathematically proved this opposite trend and concluded that 2L-Pd/Cu(111) shows greater performance towards CO oxidation.

Catalytic Asymmetric Synthesis of α-Aryl-β-Acyloxy Propanoates

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ABSTRACT

The asymmetric O-H insertion reaction of diazoesters to carboxylic acid is an ideal synthetic strategy for preparing optically active α or β-acyloxy esters, which are valuable building blocks for the construction of natural products and other biological active molecules. In this presentation, a new chiral Brønsted acid derived from carboxylic acid and chiral oxazaborolidinium ion (COBI) as activator is introduced. This acid was successfully applied as a catalyst for the highly enantioselective O-H insertion reaction of diazoesters with carboxylic acids. The reaction proceeded in good yields (up to 97%) with excellent enantioselectivities (up to 99% ee) to afford various α-aryl-β-acyloxy propanoates.

Catalytic Enantioselective Hemithioacetal Isomerization: Biomimetic Access to α-Hydroxythioesters and α-Hydroxyamides[1]

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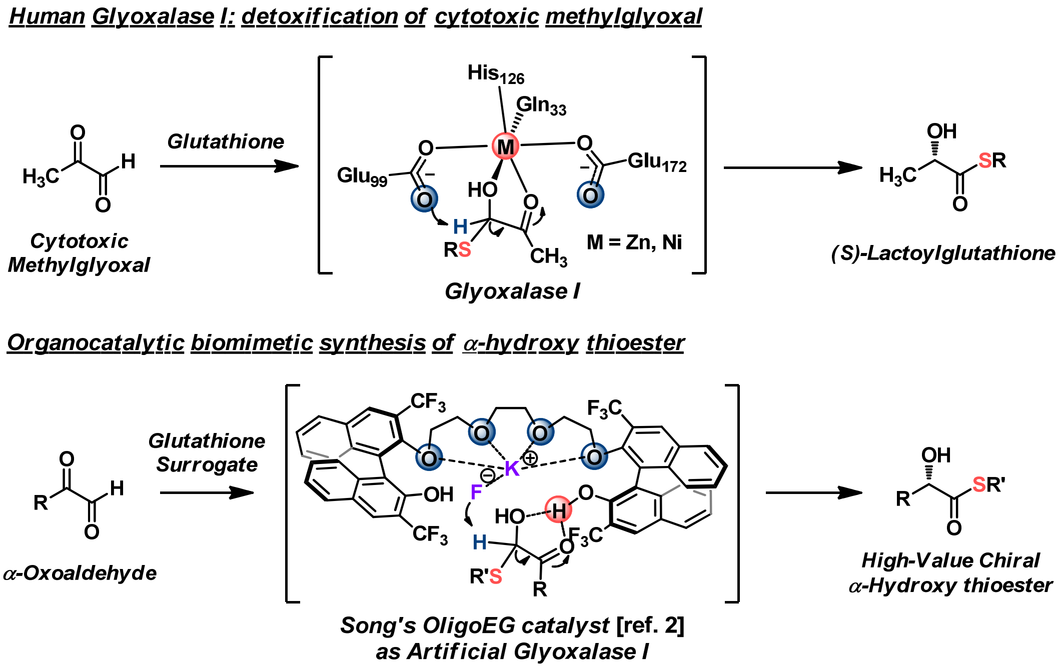
A highly enantioselective biomimetic isomerization of hemithioacetal adducts spontaneously formed from diverse 2-oxoaldehydes and thiols, affording both enantiomers of α-hydroxy thioesters, has been achieved for the first time using artificial glyoxalase I. This reaction is exceptionally enantioselective, and the α-hydroxythioester products are of high value for multiple synthetic applications, highlighted by the coupling reagent-free synthesis of several optically pure α-hydroxyamides, highly important drug candidates in the pharmaceutical industry. Like real enzymes, the enforced proximity of the catalyst and substrates by a chiral cage in-situ formed by the incorporation of potassium salt can enhance the reactivity and efficiently transfer the stereochemical information. Our strategy will provide new scientific insight for developing biomimetic catalysts, which can achieve even more than an original enzyme. Furthermore, this work would also provide a potential starting point for developing artificial enzymes which might be used for pharmaceutical uses.



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Chemical Constituents and Bioactivities from the Soft Coral *Sarcophyton cherbonnieri*

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ABSTRACT TEXT

Four new cembranoids, cherbonolides A–C (**1**–**3**) and bischerbolide peroxide (**4**), along with one known cembranoid, isosarcophine (**5**), have been isolated from the Formosan soft coral *Sarcophyton cherbonnieri*. The structures of these compounds were elucidated by detailed spectroscopic analyses, modified Mosher's method and time-dependent density functional theory electronic circular dichroism (TDDFT ECD) calculations. Compound **4** was discovered to be the first known example of a molecular skeleton formed from two cembranoids connected by a peroxide group. Compounds **1**, **3**, and **4** were found to display inhibitory effects on the generation of superoxide anion in *N*-formyl-methionyl-leucyl-phenylalanine/ cytochalasin B (fMLP/CB)-induced neutrophils, whereas the most potent compound **4** was shown to exhibit stronger activity to inhibit the generation of superoxide anion.

Chemical Tools for Detecting Cysteine Sulfenic Acids in Proteins

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Cysteine sulfenic acids are a post-translational modification in proteins caused by reactive oxygen species, particularly when a cell is under oxidative stress. Cysteine sulfenic acids are thought to be a biomarker of oxidative stress, but also a key mechanism for some redox regulation and signal transduction pathways. Since cysteines play many functional roles in proteins, understanding how oxidation to sulfenic acids may affect this function is vital for understanding the impact of oxidative stress in many diseases. Unfortunately, due to the highly reactive and unstable nature of cysteine sulfenic acids, detecting these post-translational modifications in proteins and live cells is a challenging task.

Several chemical probes have been utilised for detection of cysteine sulfenic acids based around the dimedone core. However, while they offer good selectivity, they suffer from slow reaction kinetics limiting the detection of short-lived, highly reactive cysteine sulfenic acids.[1,2]

Design of a new chemical probe utilising the ring strain of the norbornene scaffold has been explored and will be presented in this poster. The alkene functionality of norbornene reacts through a strain promoted cycloaddition with the sulfenic acid forming a sulfoxide adduct. Initial model studies on a small molecule cysteine sulfenic acid showed the ability of norbornene to rapidly trap the sulfenic acid when dimedone could not. Further studies on proteins with various functionalised norbornenes (fluorophore, biotin, alkyne, azide) have demonstrated the ability of these norbornene probes to trap cysteine sulfenic acids in proteins and will be presented.

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Cholesterol-sensing Interactions of Islet Amyloid Polypeptide with Lipid Membranes

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Deposit of human islet amyloid polypeptide (hIAPP) at the β-cells of the pancreatic islets has been associated with β-cell dysfunction and death in type II diabetes mellitus. Interaction between the N-terminal domain of hIAPP ($hIAPP_{1-19}$) and cellular membrane is a key step in the toxicity of hIAPP to the β-cells. Cholesterol is believed to play a significant role in the peptide-membrane interaction by regulating the ordering of lipids and the formation of microdomains in cellular membranes. In this study, we monitor the interactions of $hIAPP_{1-19}$ with model membranes made up of phosphatidylcholine and explore the effects of cholesterol on the binding of the peptide to the membrane, the sencondary structures of the peptide and the peptide-induced membrane damage using nuclear magnetic resonance, circular dichroism and dye leakage experiments. Our results show that the affinity of $hIAPP_{1-19}$ for the zwitterionic membranes increases with increasing fraction of cholesterol in the membranes consisting of either saturated or unsaturated fatty acide chains. The presence of cholesterol facilitates the formation of α-helical structure of the peptide and increases the peptide-induced membrane permeability. The promoting effect of cholesterol to the interaction between $hIAPP_{1-19}$ and lipid membrane is more evident in the saturated lipid membrane than that in the unsaturated lipid membrane. Different distribution of cholesterol in the saturated and unsaturated lipid membranes may be responsible for the difference between the interactions of $hIAPP_{1-19}$ with the membranes.

Cinnamon Products Meeting GMP and TGA Requirements

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Procyanidin-containing cinnamon bark extracts have demonstrated hypoglycaemic and other therapeutic properties. The use of cinnamon barks in listed (low-risk) medicines in Australia is restricted to two species (*Cinnamomum cassia* and *Cinnamomum verum*). More recently the Therapeutic Goods Administration has also placed an extra safety measure by limiting the amount of coumarin to a maximum of 0.001% in any finished product. Since most cinnamon barks contain anywhere between 0-10,000 ppm coumarin, additional steps in manufacture are now required to minimise this component, and this can have a major impact on phytoequivalence, in particular on the purported bioactive procyanidins.

As a first step in GMP we have explored the use of DNA bar coding, volatiles composition and HPTLC as a means of authenticating cinnamon bark raw materials, be they bark or extracts. The limitations of these approaches will be highlighted and contrasted to a simplified LC-MS approach, using a suite of procyanidin dimers, trimers and tetramers that appears to provide a useful analytical approach for both identity and quality. A more advanced LC-MS approach following thiolytic degradation of procyanidins provides additional detailed compositional information to ensure phytoequivalence from source to finished products.

Co-assembly into the Solid Solution or Cocrystals with Optoelectronic Properties

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ABSTRACT TEXT

Organic solution solids or co-crystals formed with two or more different materials through intermolecular non-covalent interactions are gaining increasing research attention because of their applications in optoelectronics. More interestingly, their physicochemical properties are not simply the sum of molecular properties of the constituent compounds.

First, A solid solution of two porphyrin derivatives was achieved by in-situ heating their soluble precusors mixture.[1] Organic solar cells based on the solid solution was demonstrated for the first time, resulting in a power conversion efficiency value much higher than the devices using the single component. This increase originates largely from the suitable energy level for the solid solution state, where electronic coupling between the two porphyrins occurred. Second, an easy solution self-assembly method is reported to tailor the stoichiometric stacking of perylene-TCNQ co-crystals towards different nano/microstructures by tuning the solution concentration of donor and acceptor. Distinct molecular packing structures in these two types of co-crystals largely influence their charge transporting behavior and photoresponsivity, providing valuable insight into the rational design and controllable synthesis of organic co-crystals with desired functions.[2] Last but not the least, we demonstrate the photocurrent generation of molecular heterojunction co-crystals. Theoretical calculations reveals the different charge recombination degree of these two co-crystals, indicating that molecualr stacking plays an important role in the photovoltaic effects. This work opens an avenue to develop molecular scale p-n junction cocrystals as a promising donor-acceptor contacting mode for application in organic solar cells.[3]

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Cobalt-catalyzed Synthesis of Heterocycles via C-H Bond Activation

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Heterocycles are important structural motifs in natural products, pharmaceuticals, and functional materials. New and more efficient chemical reactions and methodologies could revolutionize the research for the preparation of heterocycles. Over the past decades, transition-metal-catalyzed C−H functionalization[1] has emerged as a powerful synthetic tool for the synthesis of a wide variety of structurally complicated heterocycles without the preactivation of starting materials. As a representative earth-abundant and less toxic transition metal, cobalt-catalyzed C-H functionalization[2] has drawn much attention for the synthesis of heterocyclic scaffolds. We have developed several cobalt-catalyzed methods for the synthesis of important heterocycles such as pyrroles,[3] quinolines,[4] indenones[5] and quinoline *N*-oxides[6]. These methods provide simple and efficient routes for the synthesis of diverse heterocycle compounds.

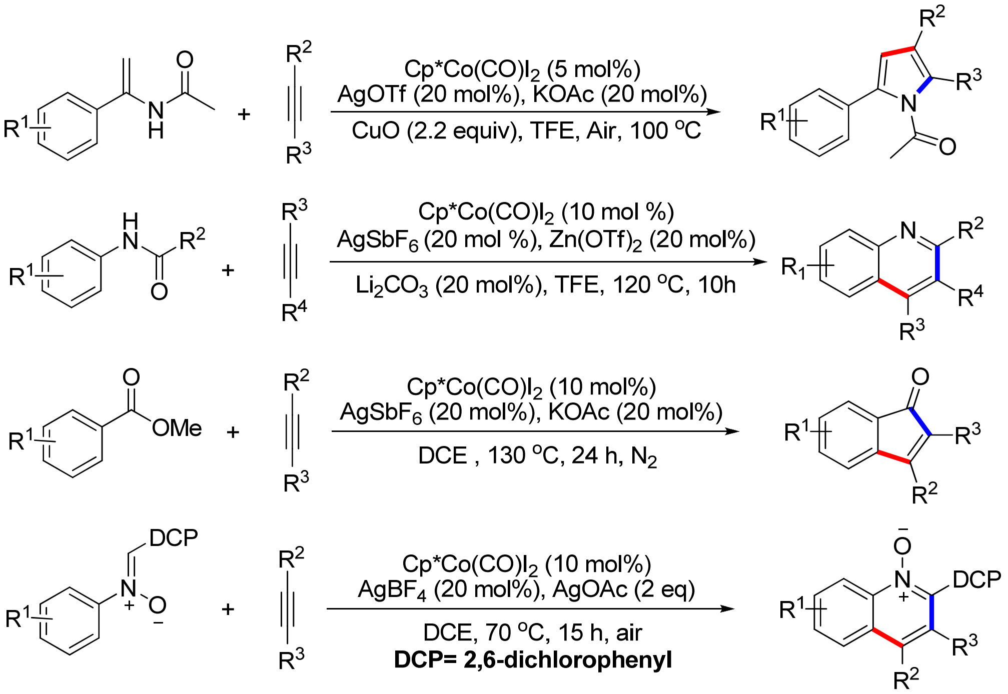

Fig. 1 Cobalt-catalyzed synthesis of heterocycles

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COLLISIONAL ELECTROCHEMISTRY OF LASER-ABLATED GOLD NANOPARTICLES BY ELECTROCATALYTIC OXIDATION OF GLUCOSE

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In metal nano-particle impact electrochemistry, a redox reaction that does not occur on a specific macroscale or microscale electrode surface, occurs at an electrocatalytic nanoparticle surface. The nanoparticle surface is only active within electron tunnelling distance of a charged surface, which is typically inactive. This scheme presents opportunities for investigating the electro-catalytic properties of nanomaterials, characterising nanoparticle suspensions and electrode surface characterisation. In this work, suspensions of amorphous gold nanoparticles are formed by laser ablation of bulk gold immersed in ultra-pure water. Electrocatalytic oxidation of glucose to gluconolactone at the nanoparticle surface is monitored by analysis of impact current transients, which are generated as the gold particle is transported towards an inert carbon fibre micro electrode.

In this novel system, electro-catalytic glucose oxidation at the bare amorphous gold nanoparticle surface is directly investigated by analysing observed current transients in terms of their peak intensity and profile. In contrast, gold nanoparticles typically used for electrochemical studies are ‘capped’ with citrate, which facilitates their formation and subsequently stabilises them against aggregation. Here, we have investigated the effect of applied potential on the electrochemical response, with reference to the electrochemistry of glucose oxidation on gold nanoparticle modified macro-electrodes. Interestingly, we found that the profile of spike transients is dependent on applied potential and that collisional events are occurring in rapid succession, which we hypothesise is related to aggregation. This work is a preliminary investigation into use of pristine nanoparticles, not poisoned by capping agents, for nano-impact electrochemistry.

COMPUTATIONAL MODELLING OF XANTHINE INTERACTIONS WITH A POLYMERIC SORBENT

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The interactions between the stationary phase and the analyte(s) are of fundamental importance in separation science. Computational modelling can be used to predict nanoscale interactions between such molecules *in silico* prior to manufacture of the sorbent potentially saving both time and money. To demonstrate this potential, the main intermolecular forces and interactions between three xanthine molecules (caffeine, theophylline, and theobromine) and Oasis HLB sorbent, were investigated using *ab initio* calculations. To model the interactions between sorbate and sorbent, a series of calculations were performed where each xanthine molecule was allowed to interact with the each individual Oasis HLB monomer; n-vinylpyrrolidone (NVP) and divinylbenzene (DVB).

Hybrid density functional theory (DFT) calculations indicate that caffeine is able to form 11 energetically favourable configurations with the Oasis HLB monomers and that whilst caffeine has a greater binding energy with the DVB monomer, it has a higher number of energetically favourable configurations with the NVP monomer. In comparison, the theophylline-monomer complexes produced 12 energetically favourable configurations and the theobromine-monomer complexes produced 11, of which the NVP configurations were found to have the greatest binding energy for both compounds due to the formation of strong hydrogen bonds between the N-H moieties of the analyte and hydrogen on the NVP monomer.

The results demonstrate that the application of computational chemical modelling to sorbent/sorbate interactions, and to chromatographic interactions can potentially reduce time and financial costs, generate new data on the fundamental interactions taking place and potentially contribute to the design of more efficient separation media.

Computational studies of non-standard carbonyl photochemistry for atmospheric simulations

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Carbonyls are some of the most photoactive, atmospherically important, and abundant volatile organic compounds (VOCs) and accurate modelling of their behaviour is crucial for any atmospheric chemistry simulation. Carbonyls are photoactive due to their C=O chromophore that absorbs solar radiation in the troposphere. Upon absorption of a photon, carbonyls have several photochemical processes they can undergo. These include the i) molecular fragmentation, the ii) Norrish Type I and iii) Norrish type II reactions, as well as photochemical reactions which undergo iv) 'triple fragmentation', or v) 'roaming', processes. While photodissocation pathways i), ii), and iii) are well studied and form the traditional basis of understanding carbonyl reactivity, the exclusion of photodissociation via iv) or v) means they are currently unaccounted for in simulations of tropospheric chemistry — and they are being increasingly shown to form significant, and often unexpected, pathways between tropospherically relevant molecules. A 'triple fragmentation' dissociation event is theoretically available to all carbonyls, and is increasingly shown as a non-negligible pathway in a range of molecules. The 'roaming' reactions a new class of reaction which bypasses a *conventional* transition state entirely — instead forming two incipient fragments which lack enough translational energy to escape each-other's van der Waals potentials, often undergoing a 'unimolecular' self-abstraction process that forms molecular products with very characteristic (and unusual) energy distributions. With computational methods, such as quasi-classical trajectories, I will determine the pressure/wavelength-dependence of *each* photodissociation pathways in a range of carbonyls, so their entire photochemistry can be incorporated into atmospheric simulations.

Computational study of the mechanism of glycosylation of L-idose derivatives

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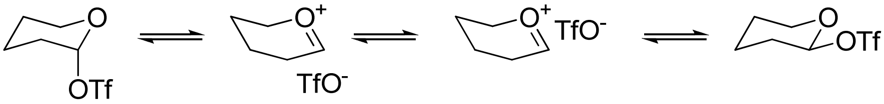
Glycosylation is one of the most fundamentally important transformations in the field of carbohydrate chemistry, but many aspects of glycosylation reaction mechanisms remain poorly understood. Recent experimental results on L-methyl idoside-forming reactions have revealed unexpected stereochemical outcomes that offer a novel means to probe the reaction mechanism.[1]

This poster will report a theoretical investigation of glycosylation reaction mechanisms involving idose and glucose derivatives. Building upon recently published computational and NMR studies,[2] which have suggested an important influence of counterions on the stability of the putative oxocarbenium ion intermediates, we have performed density functional theory calculations to explore the structures and stabilities of possible reactive intermediates and the transition states for their interconversions.



This work represents our efforts to develop, for the first time, a unified approach to the theoretical modelling of a glycosylation reaction, which considers all aspects of the mechanism including the role of the leaving group, activating agent, counterion, solvent, and conformational equilibria. Correlations with experimentally observed stereoselectivities offer a valuable test of the validity of possible glycosylation pathways.

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Controlling Sunlight to Achieve Practical Photochemical Upconversion Devices

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Sunlight is now a cost effective power source, but conventional single junction solar cells allow a portion of sunlight to pass through the cell without being captured. The extra light can be made useful with photochemical upconversion. We use simulations to show that sunlight can be directed through an upconversion device in a way that increases the contribution of triplet-triplet annihilation to photocurrent by an order of magnitude.

Photochemical upconversion utilizes the light that lies below the bandgap of a solar cell. It proceeds through a five step process, consisting of: 1. absorption, 2. intersystem crossing, 3. triplet energy transfer, 4. triplet-triplet annihilation, and 5. fluorescence. In this presentation, we target enhancement of absorption using optical devices. Improvements to absorption have a significant impact on overall efficiency because triplet-triplet annihilation has a nonlinear relationship to the triplet concentration in the device. We will show how to drive up the triplet concentration.

In a typical upconversion device, the triplet concentration is highest on the side facing the sun. It decreases exponentially as the light is absorbed through the device, until it is negligible on the back side. As a result, most of the thickness of a typical upconverting device has a low triplet concentration, which leads to low efficiency. Using a thinner, cheaper upconverter and a light director, we calculate the increase in triplet concentration that is achieved if the sunlight's optical path length through the upconverter is increased.

Conversion of agricultural residues to bicyclic compounds

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ABSTRACT TEXT

The age of fossil fuels and resources will eventually come to an end. To be prepared for this, finding alternatives to fossil resources is of major importance in all related fields. Right now 98 % of all chemicals worldwide are produced from fossil resources, even though renewable resources are readily available. To be able to harvest these renewables for chemical purposes new methodologies have to be developed, so that we are able to convert biomass derived chemicals into high-value fine chemicals and pharmaceutical precursors. This work focuses on the conversion of agricultural residue biomass into small molecules of value to the pharmaceutical industry. The conversion of biomass into bicyclic compounds will be the key finding of this research, which can ultimately form the basis of a variety of known and successful pharmaceuticals.

Copper(II)-Catalyzed C-O/C-S Bond Formation between Aryl Halides and Alkanediol/Alkanedithiol: Synthesis of Phenols and Thiophenols

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ABSTRACT

Carbon-heteroatom bond formation via cross-coupling reactions is among the important transformations in chemical synthesis, as the resulting products are useful in various applications in the fields such as medicine and industrial materials. We have been developing efficient and practical methods for the preparation of phenols, thiophenols, and their derivatives, using Cu (II)-catalyzed cross-coupling reactions. Here we wish to report recent progress in our research. First, an efficient copper-catalyzed C-O cross-coupling reaction between aryl bromides and ethylene glycol has been developed employing cheaper, more efficient, and easily removable copper(II) catalyst. A broad range of aryl bromides were coupled with ethylene glycol using catalytic $CuCl_2$ and K_2CO_3 in the absence of any other ligands or solvents to afford the hydroxyethyl aryl ethers in good to excellent yields. In this protocol, ethylene glycol has the multilateral functions as coupling reactants, ligands, and solvents. The resulting hydroxyethyl aryl ethers were further readily converted into the corresponding phenols, presenting a valuable alternative way to phenols from aryl bromides. Similarly, aryl halides were cross-coupled with 1,2-ethanedithiol under copper(II)-catalytic conditions. In this case, the resulting coupled products were *in-situ* directly converted into aryl thiols via intramolecular cleavage of $ArS\text{-}C_{alkyl}$ bond. Thus, the newly developed protocol provides a highly efficient metal-catalyzed *single-step* synthesis of thiophenols from aryl halides. It features use of readily available reagents, a simple operation, and relatively mild reaction conditions. A broad substrate scope with excellent functional group compatibility was observed and a variety of thiophenols were directly prepared from aryl halides in high yields.

Copper-Catalyzed Arylation of Benzothiazoles with Toluene Derivatives

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2-Aryl benzothiazole represents a privileged synthetic motif since many compounds containing this core structure exhibit diverse biological and pharmacologicalactivities such as antitumor, antiviral, and antimicrobial. As a consequence, many efforts have been devoted to the synthesis of such skeletons in an efficient manner. Traditionally, these compounds could be prepared from the condensation of 2-aminothiophenol with carboxylic acids or aldehydes. Nevertheless, these methods often suffered from the drawbacks including high reaction temperature, and the difficulties in synthesizing the starting materials. To overcome the drawbacks of traditional methods, there is a continuous demand for the development of efficient and environmentally benign synthetic strategies. On the other hand, toluene and its derivatives were considered to be simplest and readily available starting materials in nature, which made them highly valuable building blocks in organic synthesis. A careful literature survey revealed that reactions using toluene derivatives as benzyl precursor were very popular, thus offering a new opportunity for the formation of carbon-carbon and carbon-heteroatom bond. Additionally, using arylmethanes as acyl source was another research focus and much progress had been achieved. In this regard, we became interested in exploring novel reactions using toluene derivatives as versatile building blocks. Most recently, we have just disclosed the coupling reaction of toluene derivatives with isocyanides and carbonyl compounds, respectively. As a continuation of our previous research, herein we wish to disclose a copper-catalyzed synthesis of 2-aryl benzothiazole from benzothiazole and toluene derivatives. In this work, we have developed a novel copper-catalyzed synthesis of 2-aryl benzothiazole from readily available toluene derivatives and benzothiazole. Moreover, many mechanistic studies were also made to explain the present coupling reaction. Other features of present strategy also included the employment of simple starting materials, a broad range of substrate scope, and mild reaction conditions. As a result, the present reaction has potential to be further applied in organic synthesis.

Copper-Catalyzed Electrophilic Amination of Heteroarenes and Internal Alkynes with *O*-Benzoylhydroxylamines

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ABSTRACT:

Heteroaryl amines are important scaffolds presented in natural products, biologically active molecules and pharmaceutical targets. Various synthetic methods for formation of C(sp^2)-N bonds have been developed such as Buchwald-Hartwig amination reactions, Ullman-Goldburg type amination reactions, and transition-metal-mediated oxidative coupling reactions, which involve primary or secondary amines as nucleophilic sources. As an alternative strategy, copper-catalyzed electrophilic amination of *O*-benzoylhydroxylamines as electrophilic sources with organometallic reagents has attracted attention. For example, a variety of organometallic reagents based on organoborons, -magnesiums, -silicons, and –zincs can be efficiently aminated using electrophilic amines promoted by Cu catalyst. In our study, we investigated an efficient and mild Cu-catalyzed electrophilic amination with organoaluminum reagents in the presence of 1-3 mol % of CuCl, affording a wide range of heteroarylamines with high efficiency. Heteroarylaluminums can be readily prepared from the direct lithiation of readily available heteroarenes, followed by transmetallation with diethylaluminum chloride. In addition, we studied electrophilic amination of alkenylaluminum reagents derived from Ni-catalyzed hydroalumination of internal alkynes with diisobutylaluminum hydride (dibal-H). A broad range of enamines and tertiary amines can be synthesized in good yields. These copper catalytic protocols are efficient and practical to prepare various amine compounds.

Coreactant-free and supersensitive sensing for Cu^{2+} by graphene oxide amplified electrochemiluminescence of graphitic carbon nitrid

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Here for the first time, we present a novel electrochemiluminescence (ECL) sensor based on graphitic carbon nitride/graphene oxide (g-C_3N_4/GO) hybrid for the ultrasensitive detection of Cu^{2+}, which is a common pollutant in environmental system. The g-C_3N_4/GO shows stable ECL signal in the presence of the self−produced coreactant from oxygen reduction, and the ECL signal could be effectively quenched by Cu^{2+}, the possible ECL detection mechanism has been proposed in detail. GO can not only significantly enhance the cathodic ECL signal of g-C_3N_4 (~3.8 times), but also serve as immobilization platform for g-C_3N_4. After optimization of experimental conditions, the proposed protocol can offer a ultrasensitive, highly selective and recyclable method for the detection of Cu^{2+} with a low detection limit of 1.0×10^{-11} M and a wide linear range from 1.0×10^{-11} to 1.0×10^{-7} M. Moreover, the practicability of the ECL sensor in real wastewater samples is also tested, showing that the proposed ECL sensor could be a promising alternative method for the emergency and routine monitoring of Cu^{2+} in real sample.

Keywords: Ultra-trace Cu^{2+}; Graphitic carbon nitride; Graphene oxide; Electrochemiluminescence sensing

Correlation Between Oxidases Enzyme Activity and Total Phenolic Content

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Information regarding the relationship between enzymatic oxidases (PPO) and peroxidases (POD) and degradation of phenolic contents in herbal tea leaves is scarce. Herbal tea industries mostly use drying method especially ambient air dry to prolong the shelf life of tea leaves. In the air drying method, there is a possibility that the enzymes would degrade the antioxidative phenolic compounds in herbal tea leaves. This preliminary study focuses on the correlation between enzymatic activity and the percentage decrease in the total phenolic content (TPC) in several herbal tea leaves from tropical regions. Leaves of *Persea americana*, *Morus alba*, *Orthosiphon stamineus* and *Thunbergia laurifolia* were used in this study. The leaves were subjected to ambient air drying at 24 ± 1 °C. The change in TPC was measured. PPO and POD activity were determined from fresh tea leaves. The relationship between percentage of TPC change and PPO activity was determined with a trendline of $y = 3.1879x + 32.037$ ($R^2 = 0.9174$). The relationship between percentage of TPC change and POD activity was expressed as $y = -0.4473x + 47.193$ ($R^2 = 0.0298$). The result suggests that there is a positive correlation between PPO activity and TPC decrease in herbal tea leaves while there is no correlation between POD activity and phenolics degradation. This study could benefit the herbal tea industry by providing the most economical drying method for the best preservation of nutraceutical properties in tea leaves.

CrN Thin Films Prepared by Reactive Magnetron Sputtering for Supercapacitors

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ABSTRACT

Supercapacitors have been becoming indispensable energy storage devices in micro electromechanical systems and have been widely studied over the past few decades. Transition metal nitrides with excellent electrical conductivity and superior cycling stability are promising candidates as supercapacitor electrode materials. In this work, we report the fabrication of CrN thin films using reactive DC magnetron sputtering and further their applications for symmetric supercapacitors for the first time. The CrN thin film electrodes fabricated under the deposition pressure of 3.5 Pa show an areal specific capacitance of 12.8 mF cm^{-2} at 1.0mA cm^{-2} and high cycling stability with 92.1% capacitance retention after 20000 cycles in 0.5 M H_2SO_4 electrolyte. Furthermore, our developed CrN//CrN symmetric supercapacitor can deliver a high energy density of 8.2 mWh cm^{-3} at the power density of 0.7 W cm^{-3} along with outstanding cycling stability. Thus, the CrN thin films have great potential for application in supercapacitors and other energy storage systems.

Cu@MOF composite catalyst for Phenylboronic acid coupling reaction

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Transition metal-catalyzed carbon-carbon coupling reaction is one of the most important reactions in organic synthesis and the synthesis of fine chemical products. Here, for the first time, CuCl has been successfully immobilized into a metal organic framework (MIL-101(Cr)) to obtain a series of Cu@MIL-101 catalysts by a simple simultaneous impregnation reduction (SIR) method. This type of composite catalysts demonstrate excellent catalytic activity on the aerobic homocoupling of arylboronic acids under mild reaction conditions. XRD, ICP-MS, SEM-EDS and XPS characterizations of Cu@MIL-101 showed that the active species Cu^+ tends to be inside the catalyst and Cu^{2+} accumulates near the surface of catalyst caused by MIL-101, suggesting the contribution of a strong synergistic catalytic effect between Cu^+ and Cu^{2+} to the high catalytic efficiency. The superior utility of such composite system was also been elucidated by the broad scope of the reactants and the excellent yields of the reaction products, together with the high stability and facile recyclability of the catalyst.

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CYCLEN-BASED SEMICARBAZONE CHELATORS FOR BISMUTH-212 AND BISMUTH-213 RADIOTHERAPY

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ABSTRACT TEXT

Radioisotopes of bismuth(III) are under evaluation as potential α-emitting therapeutic agents. The energy emissions of α-particle decays are deposited over a very short distance (40-100 μm), resulting in a high linear energy transfer. The shorter path may also have the advantage of limiting toxicity to normal tissues adjacent to the tumour.

The short half-life of bismuth-212 ($t_{1/2}$ = 61 min) and bismuth-213 ($t_{1/2}$ = 46 min) radioisotopes limits their application. The β-emitting parent isotope lead-212 decays to bismuth-212 with a half-life of 10.6 h, thereby effectively extending the half-life of the α-particle decay to 11 h. Radionuclides incorporated into stable bifunctional chelators can be conjugated to targeting biomolecules such as peptides and antibodies to achieve selectivity for receptors expressed on cancerous cells.

Bismuth and lead generally assume high coordination numbers (6-10) with irregular coordination geometries depending on the character of the polydentate ligand, the donor atoms, and the solvent. Incorporation of semicarbazone pendent arms into the tetraazamacrocycle cyclen provides a N_6O_2 coordination sphere to the metal centre. The nonradioactive bismuth(III) and lead(II) complexes were synthesised. The ligand was radiolabelled with bismuth-213 at a range of concentrations and temperatures. The radiolabelled complex was stable in human serum *in vitro* out to 90 minutes and could represent an attractive alternative chelator for α-radiotherapy with bismuth radioisotopes.

Cytotoxicity diterpenoids from the cultured soft coral *Lobophytum crassum*

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In recent years, the aquaculture technique of soft corals has been considerably enhanced; therefore, researchers have been able to obtain larger amounts of soft corals, and thus larger amounts of bioactive metabolites, and have been able to engage in examining the various pharmacological activities. Recently, our continuing searching for bioactive agents from six cultured soft corals *Briareum excavatum, Lobophytum crassum, Paralemnalia thyrsoides, Sarcophyton* sp.*, Sinularia flexibilis* and *Sinularia sandensis,* we found that the EtOAc extracts of one soft coral *Lobophytum crassum* was shown to possess significantly in vitro cytotoxicity against Molt-4 cancer cell with IC_{50} value of 0.46 mg/mL. The current chemical investigation of *Lobophytum crassum* led to the discovery of two new cembrane-based diterpenoids (1 and 2) and eight known compounds (3-10). Compound 3(13-AC) exhibited the most potent cytotoxic activity against the tested eight cancer cell lines(K562, Molt-4, U937, Sup-T1, Ca9-22, LNcap, PC3, Cal-27) with IC_{50} values of 1.24, 0.46, 2.47, 0.56, 1.71, 3.57, 4.42 and 3.95 μg/mL respectively for 72 h.. The results of annexin-V/PI staining assays suggested that 13-AC induced cell death in Ca9-22 cells by inducing apoptosis. As demonstrated by JC-1 staining assay, 13-AC induced apoptosis by the stimulation of reactive oxygen species (ROS) generation and the disruption of mitochondrial membrane potential (MMP). The pretreatment of Ca9-22 cells with N-acetylcysteine (NAC), an antioxidant, inhibited ROS production resulting in the attenuation of the cytotoxic activity of 13-AC. Furthermore, 13-AC inhibited the metastatic ability of Ca9-22 cells as demonstrated by wound healing assay.

DEAROMATIVE [3+2] CYCLOADDITION REACTIONS TOWARDS POLYCYCLIC HETEROCYCLES

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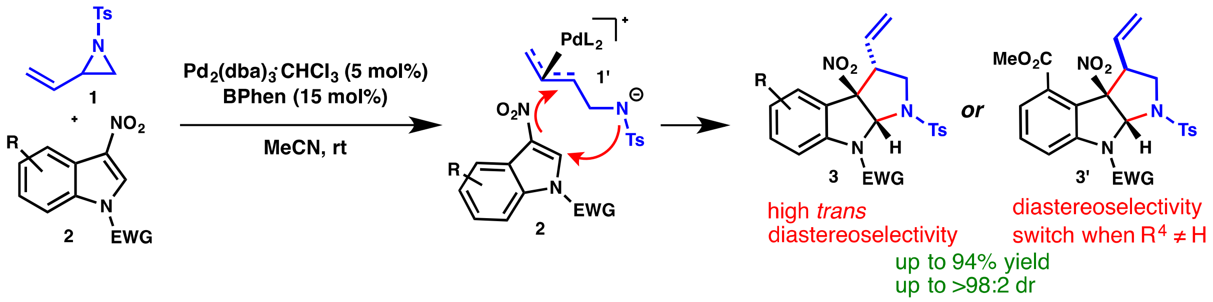
The [3 + 2] cycloaddition reaction of nitrogen-containing 1,3-dipoles with electron deficient olefins is an efficient method for the synthesis of pyrrolidine-containing compounds.[1] Less studied however, is the combination of zwitterionic 1,3-dipoles derived from vinyaziridines in combination with electron-deficient indoles in [3 + 2] dearomative cycloaddition reactions. We will present our results[2] showing that palladium(0)-catalysts can reveal a zwitterionic 1,3-dipole **1'** from *N*-tosyl-vinylaziridine **1** that can undergo a cycloaddition with highly electron-poor 3-nitro-indoles **2**. This reaction generates the biologically relevant and synthetically versatile pyrrolo[2,3-b]indole **3** moiety in a single operation. The reactions proceed to give the *trans* diastereoisomer with high selectivity, however, when a 4-substituent is present on the indole ring a complete reversal of diatereoselectivity is observed.



high *trans* diastereoselectivity

diastereoselectivity switch when $R^4 \neq H$

up to 94% yield
up to >98:2 dr

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Dehydrofluorination of hydrofluorocarbons to fluorine olefin over NiF_2-AlF_3 catalysts

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With the discharge of greenhouse gas, the problem of global climate warming is increasingly more serious, which challenges the human's living environment. According to the Kyoto Protocol, hydrofluorocarbon compounds (HFCs), including CF_3CFH_2, CF_3CH_3, CF_2FCH_3 etc., were listed in the ranks of non-CO_2 greenhouse gases. Hence, the disposal and transformation of HFCs is very significant currently. Currently, among the disposal methods of HFCs, the catalytic dehydrofluorination is an ideal route.

Dehydrofluorination of HFCs is thermodynamically and kinetically hindered, so the development of high efficient and stable catalysts is a difficulty for this process route. In our works, CF_3CFH_2 with high GWP value was served as a probe raw for model dehydrofluorination of HFCs, and the NiF_2-AlF_3 catalysts for dehydrofluorination of CF_3CFH_2 to synthesize trifluoroethylene (a useful raw material for fluoropolymer) were investigated in detail. NiF_2-AlF_3 catalysts as the solid acid with high activity for dehydrofluorination of CF_3CFH_2 were prepared, in terms of adjustment or modification on surface acidity of catalyst. In addition, the surface properties, active species and surface acidity of the catalyst were characterized by BET, XRD, Raman, UV-DRS, FT-IR, NH_3-TPD, XPS, TG-DSC and TEM/SEM-EDX techniques. Furethermore, the correlation between catalyst species and surface acidity was studied that clearly disclosed the structure-activity relationship of catalyst. The issues of catalytic reaction process and deactivation mechanism were studied, reflecting in discussing the reaction techniques and catalytic stablity for the dehydrofluorination of CF_3CFH_2. This research will not only provide a theoretical guide, but also bring the reference of industrial application in the future.

DESIGN OF A GREEN POLYMER WITH VERSATILE ENVIRONMENTALLY FRIENDLY APPLICATIONS

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ABSTRACT

A metal free synthesis of a novel polymer with rigid backbone of completely fused polycyclic rings and micro-pores was obtained. The hexaazatrinaphthylene core with electron donating nitrogens leads to interesting photocatalytic performances proved by a typical photo-oxidation of benzyamine and derivatives with full conversion and high recyclability. Moreover, we developed an organic-solvent free, environmentally friendly condition of Knoevenagel reaction catalyzed by the clean polymer itself. Contrary to normal polymers normally synthesized by C-C coupling catalyzed by heavy metals (e.g., Pd, Pt, Fe, etc.) the metal free synthesized polymer, due to the coordinative nitrogen, micropores and relatively high surface area, can pick up heavy metal (eg. Pb) from polluted water to a final concentration comparable to drinking limit. Such applications verifies the polymer for potential applications in clean energy, cleasing of water pollution and green chemistry.

This work is supported by Research Grants Council of Hong Kong SAR [Project No.: 9042087 (CityU 11303414)].

Desulfurization slags: from wastes to PFS coagulant by persulfate oxidation

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Abstract

Desulfurization slags (DSS), which contain rich iron and sulfur resources, are the main by-product generated from industrial gas desulphurization process. The special characteristics of self-heating and even spontaneous combustion as well as release of hydrogen sulfide gas in normal temperature, impose a serious environment safety problem to industrial production and public health. Therefore, it is very important to reasonably handle DSS, especially from both the viewpoints of environmental sustainability and effective resource utilization. Herein, we report the usage of DSS as the raw material to synthesize polymeric ferric sulfate (PFS) coagulant by catalytic thermal activation of persulfate method. First, FeS in DSS was oxidized into $Fe_2(SO_4)_3$ by $Na_2S_2O_8$ under heating. The condition optimization was conducted in the term of different weight ratio of $Na_2S_2O_8$/DSS, temperature, reaction time and stirring speed. Then, PFS was synthesized through the hydrolytic polymerization of $Fe_2(SO_4)_3$, and subsequently characterized by SEM, XRD, and FTIR. Finally, the coagulation performance of PFS was evaluated via the treatment of kaolin suspensions. Results showed that (1) the activation efficiency of $Na_2S_2O_8$ can be significantly improved by DSS; (2) the leaching rate of iron is up to 93.48% and no hydrogen sulfide releasing under the optimum conditions; (3) about 98% of kaolin suspensions was removed within the pH range of 5.0-11.0. In brief, the hazardous DSS can be successfully transformed into high-performance PFS coagulant through the catalytic thermal activation of persulfate.

Determination of Free and Protein-bound Sialic Acids, Neu5Ac and Neu5Gc.

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Sialic acids are ubiquitous in human biology, and are found in the highest concentration in the central nervous system. They are found mostly in their protein-bound form, glycoproteins and gangliosides, with the remainder present as free sialic acids. Sialic acids have been shown to be essential for neuronal development in infants, and although humans can synthesize Neu5Ac from simple carbohydrates, the enzyme involved may be unable to keep up with demand in growing infants. It has been clearly demonstrated that breastfed infants display long term cognitive advantages, in comparison to formula fed infants, and there is a direct correlation between the duration of breast feeding and that advantage. In addition, there is evidence to show that sialic acid levels in human plasma show a measurable and distinct change when disease, including cancer, is present. There is also evidence to show abnormally elevated plasma concentrations of the sialic acids, especially Neu5Ac and Neu5Gc, in adults with cancer. This has led us to analyse a selection of Australian infant milk formulae for the presence and concentration of both Neu5Ac and Neu5Gc, for any potential nutritional differences. We have incorporated a method that is both efficient and cost effective, for both plasma, and infant formula. This method utilises an ion-pairing agent and reverse phase HPLC with UV analysis to determine the concentration of both free and protein-bound Neu5Ac and Neu5Gc.

Development of an Ultra High Performance Liquid Chromatography (UHPLC) method for the determination of organic UV-absorbing components in sunscreen products on the Australian market.

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ABSTRACT TEXT

In response to recent public concern over sunscreens effectiveness, TGA Laboratories analysed 32 sunscreens available on the Australian market for their content of active ingredients against the requirements listed in the Australian regulatory guidelines for sunscreens (90.0% - 120.0% of label claim). A single UHPLC-based method was developed that allowed analysis of 11 organic UV-absorbing components used in the majority of Australian sunscreen products. The method allowed fast analysis of actives with a wide range of calculated log P values (3.6 – 15.3) and was found to be suitable for a wide range of sunscreen sample matrices. With fit for purpose validations performed, all actives were found to be linear in the range of 25% - 200% of median concentration range in the samples tested.

DEVELOPING PHOTOSENSITIVE DROPLETS FOR CHEMOPROPULSION

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The ability to selectively transport chemical species in a controlled fashion, typically against chemical and electrochemical gradients, has been the cornerstone of the development of complex natural systems.[1] To emulate this biological transport process, synthetic "chemopropulsion" systems have been developed. In recent years, total control of the motion has become the biggest challenge in chemopropulsion systems. The use of light as an external stimulus seems to be the most promising way to realize this goal. In 2015, Florea *et al.* developed an photosensitive aqueous solution with a spiropyransulfonic acid and partly controlled the movement of a lipophilic droplet on this solution by light (photo-chemopropulsion).[2]

We have developed a series of photoactive droplets using spiropyrans along with various acids in organic solvents. The movement of these droplets on or in pure water or surfactant solution can be totally controlled by light. In this paper, we show how the direction of droplet movement towards or away from light is determined by the composition and chemistry of the droplet mixture. To the best of our knowledge, this is the first work that realizes the photo-controlled motion of a droplet in 3D, which has promising applications in the fields of chemical cargo transport and drug-delivery.

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Development Radiochemical Separation to Determine the Model Age of Uranium

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ABSTRACT Determination of the 'model' age (i.e., time since processing) of unknown nuclear material, coupled with studies of uranium isotopic signatures, elemental and anion impurities, as well as other material characteristics, helps to reveal the origin and processing history of the material to allow its identification for nuclear forensic purposes. ANSTO's Nuclear Forensic group has participated in both the fourth and fifth Nuclear Forensic International Technical Working Group (ITWG) inter-laboratory collaborative material exercises (CMX); CMX-4 in 2014 and CMX-5 in 2016. Since the model age is a key nuclear forensic signature, these exercises required that ANSTO develop radiochemical separation procedures for the measurement of ^{234}U (^{234}U~10^{-6} g) and very low thorium (^{230}Th~10^{-11}g) isotopes in solutions of high purity enriched uranium oxide samples. Measurement of ^{230}Th/^{234}U isotopic ratio using alpha spectrometry allows the calculation of the model age of the sample. The radiochemical separation method applied in CMX-4 however gave a result with a two year discrepancy between the analytically derived age and that of the purported age supplied by the exercise administrators. This paper describes the lessons learned from CMX-4, and the introduction of additional separation steps during the procedure applied in CMX-5, enabling a more reliable measurement of the uranium and thorium isotopes to determine the model age of the uranium samples.

DEVELOPMENT OF BACTERIAL CELLULOSE/CHITOSAN/SILVER NANOPARTICLES COMPOSITE AS WOUND DRESSING

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ABSTRACT TEXT

There has been an increasing interest in the use of bacterial cellulose (BC) as wound dressings due to its biocompatibility, high moisture content and unique nanofibril network morphology, mimicking the extracellular matrix. However, the applications of BC in the field of biomedicine have been delimited by to its lack of antimicrobial activity essential in promoting normal wound healing. In this study, chitosan (Ch) and silver nanoparticles (AgNPs) were used as reinforcement materials to improve the characteristics and structure of BC, and subsequently imparting antimicrobial property to it. Chitosan, an amino polysaccharide, was prepared thru deacetylation of chitin extracted from waste materials, particularly shrimp shells. On the other hand, AgNPs were green-synthesized using aqueous pineapple leaf (Ananas comosus) extract and ascorbic acid. UV-Vis spectrometry indicated the formation of AgNPs, exhibiting surface plasmon absorption at 440-460 nm. FTIR spectrum of the composite indicated the intermolecular interaction between BC and Ch. SEM images showed a well-organized three-dimensional network structure of BC/Ch/AgNPs film. BC/Ch/AgNPs composite exhibited significant inhibition against *S. aureus* and *E. coli*. Benzalkonium chloride (Bcl), a cationic surfactant widely used as topical antiseptic agent for wounds, was selected for drug release studies. It was revealed that BC/Ch/AgNPs composite has the ability to sustainably release Bcl over a period of time, critical for wound healing. Overall, the results suggest that BC/Ch/AgNPs composite could be a promising wound dressing material.

DISCOVERY AND DESIGN OF NOVEL *EC*DSBA INHIBITORS USING FRAGMENT-BASED DESIGN STRATEGIES. A NOVEL METHOD TO OVERCOME MULTIPLE DRUG RESISTANCE.

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Bacterial resistance to antibiotics has become a major global concern with numerous bacteria now resistant to almost all current antibiotics.[3] This highlights the urgent need for new antibacterials with novel mechanisms of action. Targeting bacterial virulence rather than bacterial growth is a new approach to overcome drug resistance.[4] DsbA is a bacterial dithiol-disulfide oxidoreductase enzyme which is responsible for disulfide bond formation in Gram-negative bacteria such as *Escherichia coli*, *Burkholderia pseudomallei* and *Vibrio cholera.* DsbA plays an essential role in the folding of numerous virulence factors and is a promising novel anti-virulence target.[5]

Screening of the Monash fragment library identified multiple scaffolds that bind to *E. coli* DsbA with weak affinity.[6] Ongoing optimisation and development of a phenylthiazole class is presented where we optimise properties, expand at multiple vectors and present the screening cascade which includes solubility measurement, biophysical binding assays and collection of structural data on DsbA-fragment complexes. A number of compounds with improved affinity and properties have been developed as *E. coli* DsbA inhibitors.

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Development of Phosphine Oxide Catalyst

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ABSTRACT

In the field of organic chemistry, phosphine oxides have generally been viewed as undesirable nuisances since they are often formed as reaction by-products or result from undesired oxidation of a phosphine catalyst or ligand, and must ultimately be separated from the desired reaction product. However, recent research has shown the potential utility of phosphine oxides as catalysts in a variety of selective reactions. We have been active in this area and have focused on the development of new phosphine oxide-catalyzed reactions such as the application of triphenylphosphine oxide (TPPO) as a Lewis base catalyst in reduction reactions, and the use of 3-methyl-1-phenyl-2-phospholene 1-oxide (MPPO) as a catalyst in intra- or inter- molecular reactions. Herein, we will introduce three recently developed methods that involve phosphine oxides as catalyst: (1) TPPO-catalyzed reductive alpha-halogenation reactions, (2) MPPO-catalyzed chromatography-free amide formation reactions, and (3) Intra-molecular one-pot/three-step tandem reactions that can form pyrroline, tetrahydropyridine, and larger ring structures.

Development of potent and selective enzyme inhibitors via fluorine utilisation

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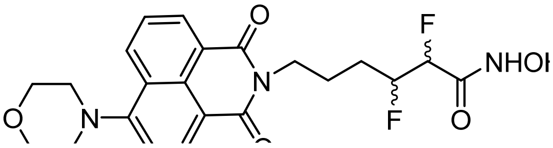
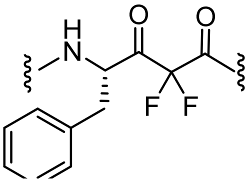
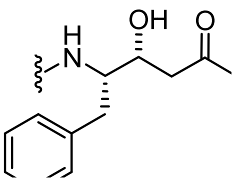
Enzymes play a crucial role in the body; they catalyse critical processes and ensure homeostasis. However, in various disease states, enzymes are upregulated or subject to mutations which cause them to act irregularly and stimulate disease progression. As such, they are a medicinally important drug target and the design and use of enzyme inhibitors has become a prominent method to halt irregular enzyme activity and alleviate disease.

Fluorine is a very useful tool for the enhancement of enzyme inhibitors. It provides several advantages including conformational control, increased lipophilicity, increased metabolic stability and the ability to mimic electron distributions of transition state structures. This research will explore the breadth of fluorine's applications with respect to inhibitors of two medicinally significant enzymes: histone deacetylase (HDAC) and beta secretase-1 (BACE-1) implicated in cancer and Alzheimer's disease respectively. In the first case the main focus will be to utilise fluorine to impose conformational restriction to improve selectivity. In the second case the aim will be to exploit fluorine to develop transition state mimics to improve potency.







HDAC inhibitors:

Different fluorine stereochemistry causes the molecule to favour different conformations

BACE-1 inhibitors:

Fluorine gives a good mimic of the transition state of peptide hydrolysis

Developments of Fluorescent Reagents for the Selective Detection of Neurotransmitters

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Neurotransmitters manages a wide range of cognitive functions, which include motivation, behavior, learning, and memory. The amount of dopamine, which is one of the famous neurotransmitter, in the human brain is an important factor in various diseases, and is one of the markers used in the diagnosis of several conditions related to neurotransmitters, including Parkinson's disease. Consequently, there is a strong need to develop efficient and rapid methods that can be used to selectively determine and continuously sense changes in the dopamine levels.

We report the development of (E)-2,2'-(5-(2-(4-(dicyanomethylene)-6-methyl-4H-pyran-2-yl)vinyl)-2-hydroxy benzylazanediyl)diacetic acid Fe(II) complex (**1-Fe^{2+}**), a fluorescent reagent that can be used to detect dopamine. **1-Fe^{2+}** was constructed using the cyanopyranyl group as the fluorophore and an Fe^{2+} complex both as the ligand exchange site and fluorescence quenching moiety. In contrast to the weak fluorescence emission of **1-Fe^{2+}** in the absence of dopamine, a much stronger fluorescence emission was observed following the addition of dopamine owing to the release of Fe^{2+} from compound **1**, which indicates significant fluorescence enhancement and the binding of Fe^{2+} to dopamine. The fluorescence intensities of the reagent were plotted as a function of the dopamine concentration and a good linear relationship was observed. The reaction of **1-Fe^{2+}** with dopamine was not affected by the presence of foreign substances, thereby allowing for the highly selective detection of dopamine. The experimental results clearly showed that **1-Fe^{2+}** is a good dopamine indicator, and it can be widely employed in dopamine detection protocols.

DFT Investigation of Insertion Reactivity of N-Heterocyclic Carbenes

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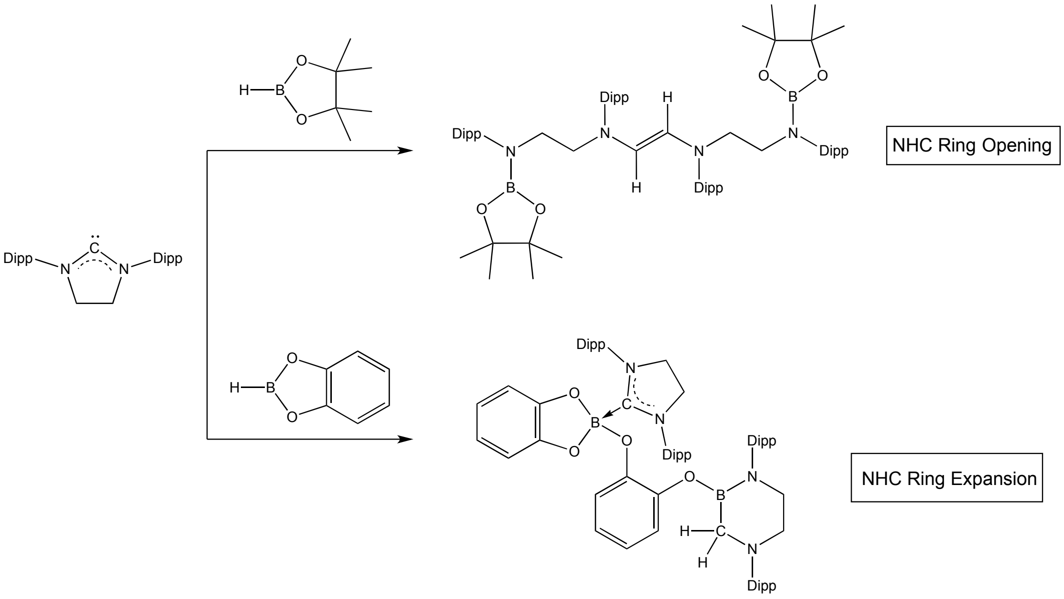
N-heterocyclic carbenes (NHCs) are well-known as robust ligands, but have recently been observed to undergo ring expansion reactions, with the insertion of main group element hydrides into the five-membered ring. Ring expansion reactivity potentially impacts catalytic and synthetic pathways involving NHCs. Here we will report results from a computational study of recently reported experimental observations of ring expansion, which have expanded the type of reactivity, and nature of N-heterocyclic ring systems for which ring expansion has been observed.

Gandelman[1] and co-workers have reported the ring expansion of nitrenium ions, which are isoelectronic to NHCs. Ring expansion was achieved by reaction with a PR_2^-, leading to insertion of P into the ring. Separately, Radius and Marder[2] have reported the ring expansion of saturated NHC^{Dipp} with catecholborane. Curiously, the reaction of saturated NHC^{Dipp} with pinacolborane (an analogue of catecholborane) unexpectedly causes degradation of the NHC ring producing a dimer.[3]

The reactivity of NHCs and boranes has been explored using DFT methods. Preliminary calculations indicate that NHC ring insertion is thermodynamically favourable with catecholborane, however, unviable with pinacolborane.



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Discovery and synthesis of novel peroxisome proliferator-activated receptor δ agonists

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Peroxisome Proliferator-Activated Receptor δ (PPARδ) has recently come into the focus as a re-emerging drug target for the treatment of associated diseases such as metabolic syndrome as its activation alters glucose and lipid metabolism through a transcriptional regulation and results in beneficial pharmacological actions, typically an exercise mimic. We synthesized novel PPARδ ligands and an efficient synthetic route to these analogs was also developed. Surprisingly, some of compounds were potent and selective hPPARδ agonists with 200-fold selectivity over the other two subtypes, namely, hPPAR δ and hPPARδ. Some selective PPARδ ligands showed good bioavailability and in vivo efficacy. These results suggest that our novel PPAR δ agonists could be promising candidates for inflammation and metabolic diseases.

Diverse reactions of thiophenes, selenophenes and tellurophenes with strongly oxidizing I(III) PhI(L)$_2$ reagents

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Hypervalent iodine reagents are effective in oxidizing and delivering groups to transition metals and main group elements (Kniep, 2012; Yuan, 2016). _ENREF_12 In previous work, our group has reported the unusual reactivity of 2,5-diphenyltellurophene with $[PhI(4\text{-}DMAP)_2]^{2+}$ with an electrophilic aromatic substitution occurring at the 3-position of tellurophene via a Te(IV) intermediate, where pyridine nitrogen atoms are acting as the electrophile (Aprile, 2015). Reactions of group 16 heterocycles thiophenes, selenophenes and tellurophenes with hypervalent iodine oxidants, PhI(OAc)(OTf) and $[PhI(Pyr)_2][OTf]_2$ (Pyr = pyridine) are presented here. Oxidative processes were observed in all reactions. However the +4 oxidation state is only observed in the reaction of tellurophene with PhI(OAc)(OTf) while a variety of electrophilic aromatic substitutions are observed in others. In general, an electrophilic aromatic substitution of either –IPh or pyridine on the ring was observed when a C-H unit is available on the ring. When all 4 positions of the ring were blocked, the reaction with PhI(OAc)(OTf) gives acetic and triflic anhydride as the identifiable oxidative by-products, while $[PhI(Pyr)_2][OTf]_2$ gives pyridine electrophilic aromatic substitution onto the peripheral rings.

Domino Kornblum-DeLaMare/aza-Michael reactions of 3,6-dihydro-1,2-dioxines

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3,6-Dihydro-1,2-dioxines are a type of endoperoxide which are known to undergo a range of reactions and are useful for the incorporation of 1,4-dioxygen functionality into organic molecules. Most chemical processes involving 1,2-dioxines proceed through an initial Kornblum-DeLaMare rearrangement which gives highly reactive 4-hydroxyenone intermediates. These enones can undergo dehydration to furans under moderately acidic conditions and also undergo facile rearrangement to 1,4-diketones with amine bases. When heated with primary amine bases, pyrroles result through a Paal-Knorr reaction which involves a domino Kornblum-DeLaMare rearrangement followed by rearrangement to a 1,4-diketone. We have discovered that at low temperature, the intermediate enones undergo a reversible aza-Michael addition giving 4-hydroxy-3-aminoketones which can be isolated in excellent yield. To avoid the retro-aza-Michael reaction, the addition products were reduced using sodium or zinc borohydride yielding 3-amino-1,4-diols. Work is underway to convert these aminodiols through to HPA-12, which is an inhibitor of the cytosolic ceramide transporting protein with the potential to affect intracellular ceramide and sphingomyelin concentrations.

EFFCIENT METAL-FREE SYNTHESIS OF PERFLUOROALKYLATED FLUORENES

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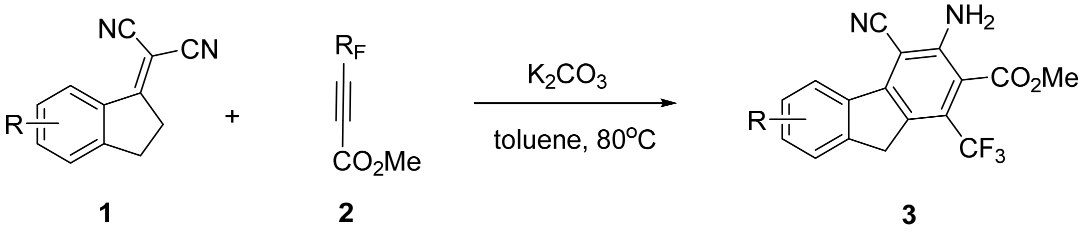
ABSTRACT TEXT

Fluorene is one of the simplest motifs in polycyclic aromatic hydrocarbons, and its derivatives have found broad applications in materials science, pharmaceutical chemistry and organic synthesis[1]. In recent years, the photoelectrical potential of fluorene and related derivatives has become well recognized. Herein we report a novel and efficient metal-free method for the synthesis of perfluoroalkylated fluorene derivatives involving a reaction of 2-(2,3-dihydro-1*H*-inden-1-ylidene)malononitriles[2] **1** and methyl perfluoroalk-2-ynoates **2**. A series of perfluoroalkylated fluorene derivatives **3** were synthesized in good to excellent yields (Scheme 1 and Table 1).



Scheme 1

Table 1 Synthesis of perfluoroalkylated fluorene derivatives **3**[a]

Entry	R	R_F	Product **3**	Yield (%)[b]
1	H	CF_3	**3a**	96
2	5-Br	CF_3	**3d**	92
3	H	C_2F_5	**3b**	94
4	5-Br	C_2F_5	**3e**	93
5	H	C_3F_7	**3c**	94
6	5-Br	C_3F_7	**3f**	90

[a] Reaction condition: **1** (1 mmol), **2** (1.2 mmol), K_2CO_3 (0.1 equiv) were stirred in toluene (5 mL) at 80 °C for 6 h. [b] Isolated yields.

ACKNOWLEDGEMENT

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EFFCIENT SYNTHESIS OF TRIFLUOROMETHYLATED 5*H*-SPIRO[FURAN-2,3'-INDOLIN]-2'-ONES

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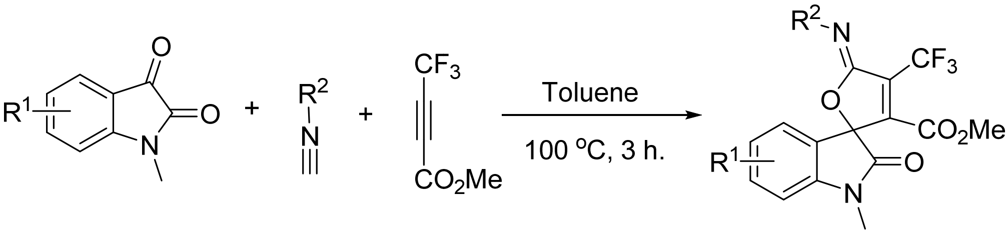
ABSTRACT TEXT

Indolinone is an important class of heterocyclic compounds. The structural units widely present in natural products, drug molecules and functional materials[1]. Numerous studies show that, when introduction of fluorine atom(s) into the heterocyclic compound, it's physical, chemical and physiological properties could be improved significantly[2]. Thus, here we report an efficient method for the synthesis of trifluoromethylated 5*H*-spiro[furan-2,3'-indolin]-2'-one derivatives **4** involving a reaction of *N*-substituted isatins **1**, isocyanides **2** and methyl 1,1,1-trifluorobut-2-ynoate **3** (Scheme 1 and Table 1).



1 **2** **3** **4**

Scheme 1

Table 1 Synthesis of trifluoromethylated 5*H*-spiro[furan-2,3'-indolin]-2'-one **4**[a]

Entry	R^1	R^2	Product **4**	Yield (%)[b]
1	H	$(CH_3)_3C$	**4a**	93
2	H	Cyclohexyl	**4b**	82
3	H	Ph	**4c**	89
4	5-Br	$(CH_3)_3C$	**4d**	83
5	5-CH_3	$(CH_3)_3C$	**4e**	90

[a] Reaction condition: **1** (1 mmol), **2** (1.5 mmol) and **3** (1.5 mmol) were stirred in toluene (5 mL) at 100 °C for 3 h. [b] Isolated yields.

ACKNOWLEDGEMENT

We are grateful to the National Natural Science Foundation of China (Grant Nos. 21672138, 21272152, 21542005) for the financial support.

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Egg Shell Membrane Templated Nickel Molybdate for supercapacitor electrodes

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Urgent demands for sustainable energy sources have been triggered due to population growing and environmental concerns. Renewable energy is generated from natural sources including sunlight, wind and water and energy storage from these intermittent sources is required. Supercapacitors are a superior storage alternative as they provide higher power and energy density than traditional batteries or conventional dielectric capacitors. Investigation of new electrode materials is essential to improve storage capacity and charge transfer performance.

Binary transition metal oxides (BTMOs) are promising materials for high performance supercapacitors due to multiple, easily accessible oxidation states and high electrical conductivity. $NiMoO_4$ is attractive due to the chemical stability, low cost and enhanced electrochemical performance of the material. Improvements in electrode performance could be achieved by template addition inducing increases in specific surface area, the electrode/electrolyte contact area and resulting in particle shapes that enhance material conductivity. Egg Shell Membrane (ESM) is a novel template that is renewably sourced, fibrous, easily removed and may result in formation of elongated particles in a porous ‘mesh-like’ structure, simultaneously increasing material surface area and conduction.

$NiMoO_4$ with ESM template was synthesised from simple salts by hydrothermal combustion. The ESM template material showed increased specific surface area, a relatively large pore volume range, and a much more porous structure than material synthesised without template. The template material had excellent performance characteristics with the specific capacitance increased 400 % compared to non-template $NiMoO_4$. Improvements in electrochemical performance correlated with increased addition of ESM.

Electrochemical DNA biosensing based on graphene/ molybdenum disulphide/gold nanoparticle composites

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ABSTRACT TEXT

A sensitive thin film for the detection of DNA hybridization was established. The platform was prepared based on the modification of glass carbon electrode with graphene (Gr) and analogue graphene (molybdenum disulfide) composite (Gr/MoS_2) decorated with gold nanoparticles. The composite of Gr/MoS_2 was synthesized via a hydrothermal method by the use of polyethyleneimine (PEI) as the dispersant. Gold nanoparticles were in situ synthesized on the surface of the Gr/MoS_2 composite, which were employed to anchor single probe DNA molecules. The electrochemical properties of the composites were investigated via CV and EIS. DNA immobilization and hybridization on the prepared functional film were studied and detected via cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under the optimized conditions, the DNA biosensor shows a good linear relationship between 0.01 pM to 100 pM with a limit of detection of 0.005 pM. The functional hybrid film displays good stability during repeated regeneration and hybridization cycles.

Electrochemical Plating of Au-Cu Alloy Films for MEMS Sensor Applications

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ABSTRACT TEXT

In recent years, Au has become a promising material as functional movable structures in MEMS accelerometer sensor, because Au density is ca. 10 times higher than that of conventional Si. However, Au is known to be a soft material. Yield stress of bulk Au is reported to be 55~200 MPa. The mechanical strength and grain growth become critical concerns in miniaturization of the pure Au-based MEMS sensors. Alloying of Au is expected to enhance the mechanical strength and suppress the grain growth.

In this study, Au-Cu alloy films were fabricated by pulse electroplating. Grain size of Au-Cu alloy was ranged from 5.6 to 8.7 nm by changing the pulse peak current density (Ip) from 3 to 10 mA/cm^2. Grain refinement was attributed to the higher Ip, because high adatoms population and high overpotential can be achieved by applying higher Ip. The Cu content increased from 5.4 to 21.0 wt.% with increasing Ip. Moreover, Lower Cu content is advantageous for the MEMS accelerometer. The Cu content of Au-Cu alloy film prepared by pulse electroplating was much lower than that prepared by constant current electroplating, which was attributed to galvanic displacement of Au during the pulse off-time.

The mechanical properties of the materials in micro-scale are usually different from those of the bulk materials. Therefore, micro-mechanical properties of Au-Cu films were evaluated by micro-compression tests. The ultra-high compressive stress of 1200 MPa was achieved due to its ultra-fine grain and chemical composition change of Au-Cu alloy.

Electrochemiluminescence immunosensor for microcystin based on MoS_2 nanosheets

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Water pollution caused by microcystins is increasing all over the world. It is important to develop new methods of determining microcystins. An electrochemiluminescence (ECL) immunosensor for microcystin-leucine- arginine (MCLR) was developed in this paper. Layered MoS_2 nanosheets as the carriers of bovine serum albumin coupling MCLR (MCLR-BSA) were modified onto the surface of a glassy carbon electrode. Large amounts of CdSe quantum dots (QDs) were loaded on graphene sheets (GS) to prepare composite (QDs-GS). The composite was used to label antibody against MCLR (Ab) to obtain composites (Ab-QDs-GS) which can amplify ECL signal. The immunosensor was incubated with 5 μL Ab-QDs-GS suspension and 5 μL different concentration MCLR solution for 1 h. MCLR in solution competed with MCLR-BSA modified on the electrode surface for the limited binding sites of Ab labeled with QDs-GS to form the immune-complex. ECL experiment was performed with a MPI-A analyser, an immunosensor as working electrode, a platinum wire as counter, and a Ag/AgCl as reference electrodes. The immunosensor generated ECL signal in 0.1 M phosphate buffer solution containing of 0.1 M $K_2S_2O_8$. The potential window was from 0 to -1.5 V with a scan rate of 100 mV/s. The ECL intensity of the immunosensor was decreased with the increases of MCLR concentration and was linearly dependent on the MCLR concentration from 0.0050 to 100 μg/L with a detection limit of 0.003μg/L. The immunosensor was applied in determining MCLR in real samples and satisfactory results were obtained.

Electro-generated ROS for the oxidative dissolution of V_2O_3 in alkaline solution

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ABSTRACT TEXT

In-situ electrochemical generated reactive oxygen species (ROS) are often used for environmental remediation in advanced oxidation process under acid conditions. In the present study, the oxidation of V(III) (vanadium oxide) to V(V) (vanadate), a critical pre-treatment process for vanadium utilization, is efficiently achieved by the reactive species produced via two-electron ORR on the N-doped carbon felt cathode in alkaline media. Nitrogen-containing functional groups appeared after N-doped treatment, which highly enhance the hydrophilic behaviour and electro-catalytic properties of HO_2^- generation. In this study, novel electro-oxidation mechanism on the cathode is presented for vanadium transformation. It was determined by radical quenching experiment that 43.5% V(III) was oxidized by HO_2^- and 56.5% was owning to the hydroxyl radicals generated from vanadium self-induced electro-Fenton-like reaction, respectively. The V_2O_3 solid particles can be well in-situ oxidized on the surface of cathode because of the V_2O_3 adsorbed on the carbon felt surface during the EAOPs. Therefore, this novel V_2O_3 electro-oxidation mechanism found for the ROS under alkaline conditions supplements the fundamentals of heavy metal transformation in electrochemical processes and serves a promising solid waste treatment method.

Electronic Spectra of Weakly Bound Diacetylene (HC4H+) Complexes in the Visible and Ultraviolet Regions

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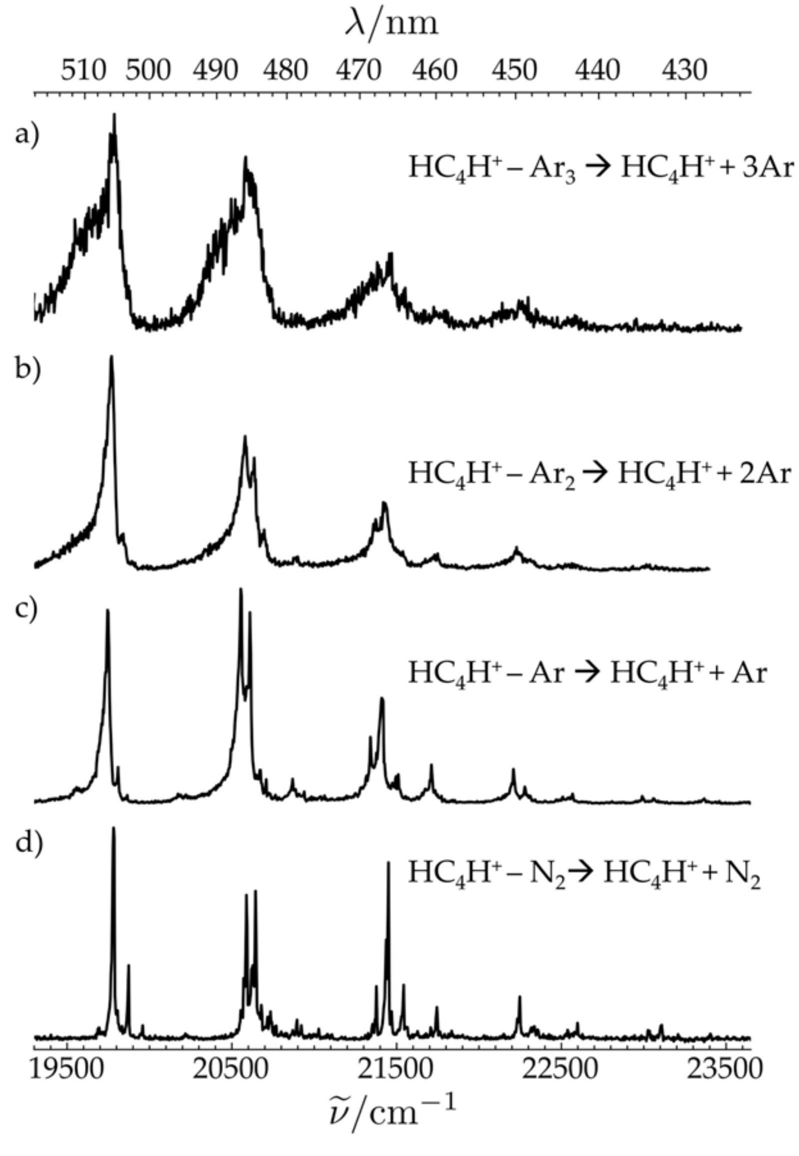
Electronic spectra of the $\tilde{A}^2\Pi_u \leftarrow \tilde{X}^2\Pi_g$ transition of weakly bound HC_4H^+-Ar_n (n = 1-3) and HC_4H^+-N_2 complexes have been obtained in the 425-530 nm range through vibrational predissociation spectroscopy using a tandem mass spectrometer. The origins of these bands are observed at 19 746, 19 770, 19 786, and 19 782 cm^{-1} for HC_4H^+-Ar, HC_4H^+-Ar_2, HC_4H^+-Ar_3, and HC_4H^+-N_2, respectively. The vibronic structure is assigned using time-dependent density functional calculations (TD-DFT), and the dominant progression in the visible range is due to the C-C symmetric stretching mode (ν_3), which lends intensity to the C≡C-C antisymmetric bending vibration (ν_7) due to Fermi resonance. The $C^2\Pi_u \leftarrow X^2\Pi_g$ transition of HC_4H^+-Ar has been recorded from 275-350 nm with a measured origin at 29 762 cm^{-1}.



ELUCIDATING HUMAN HSP47 BINDING AND RELEASE BEHAVIOUR USING SITE-DIRECTED MUTAGENESIS

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ABSTRACT

Collagen biosynthesis in the cell is assisted by many proteins acting as molecular chaperones. Abnormalities in collagen expression led to many types of diseases. Thus, thorough understanding of the specific molecular chaperone can assist novel treatment strategies for these collagen-related diseases. Heat shock protein 47 (HSP47) is a unique and important collagen-specific molecular chaperone in collagen biosynthesis. The molecular mechanisms for HSP47 binding to and release from collagen in the cells has just been proposed (Widmer et al., 2012; Oecal et al., 2016), using canine HSP47 as model. However, the mechanisms in human HSP47 is still unknown. We used human HSP47 gene cloned into an *E. coli* expression vector, for *in vitro* mutational analysis. Histidine residues are targeted, as the HSP47-collagen dissociation pH is similar to histidine dissociation constant (pK_a). Homology modelling of human HSP47 using the crystal structure of canine HSP47 in complex with trimeric collagen model peptides was used to guide mutagenesis experiments. Alanine scanning mutagenesis, coupled with collagen binding assay and circular dichroism (CD) spectroscopy revealed that several His-to-Ala mutants (H220A, H335A, H368A) showed perturbed binding and/or structural integrity relative to wild-type. These suggest the potential involvement of the particular His residues in collagen binding and/or release. These mutants are currently being investigated using ELISA-based collagen binding assay to further assess their binding strength. Then, the secondary structure transition induced by pH will be thoroughly investigated using CD spectroscopy.

Enantiospecific Synthesis of γ-Lactones via Cyclopropanation and Benzylation of Levoglucosenone

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Levoglucosenone (6,8-dioxabicyclooct-2-en-4-one, LGO) is the major product formed from the acid-catalysed pyrolysis of cellulose. Production of LGO on a tonne scale has recently been achieved by Melbourne based Circa Pty Ltd., thus providing a new chiral pool entry which may enable environmental and economic benefits for selected products.

To develop new uses for LGO, we have investigated the Johnson-Corey-Chaykovsky cyclopropanation of 3-aryl derivatives of LGO. We found that the key to high yields and selectivity for 1,4-addition giving cyclopropanation was the combination of trimethylsulfoxonium iodide with tetramethylguanidine in DMSO. Excellent yields and diastereoselectivities for a range of aryl substituents were obtained. We have also developed a synthesis of (3*R*,5*S*)-3-benzyl-5-(hydroxymethyl)dihydrofuran-2(3*H*)-one (BHMF), a precursor to the antiviral protease inhibitor indinavir and related pentanamides. The successful method involved aldol condensation between benzaldehyde and dihydrolevoglucosenone followed by reduction to the ketone, epimerisation and Baeyer-Villiger oxidation. The approach has significantly abbreviated the synthesis of BHMF compared to current methods, while also showing applicability to production of other 3-arylmethyl analogues.

Engineering Disorder into Heteogenite-Like Cobalt Oxide by Phosphate Doping: Implications for the Design of Water-Oxidation Catalysts

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Metal oxides are amongst the best known and most extensively studied water oxidation catalysts. Despite the success of these materials, understanding the relationship of structure to function has been very challenging. It has been noted that many metal oxide water oxidation catalysts function best in a proton accepting electrolyte, such as a borate or phosphate buffer. However, these same electrolytes are known to significantly affect the metal oxide structures by imparting a level “disorder” or “molecular nature” to the materials. In our 2015 study, we have synthesised a series of “heterogenite–like” cobalt oxides with different levels of phosphate doping (0 – 9 %P). Our synthetic method enables us to make “bulk materials” whose structural properties (as observed by XAS and TEM) mimic those observed directly on electrode surfaces. The most disordered materials were most reactive for sacrificial oxidation but were less effective as water oxidation catalysts. These results help us understand how disorder changes the thermodynamic stability of metal oxides and how this impacts on efficiency for water oxidation.

Enhancement of Electrokinetic Behaviour and Performance of Microbial Fuel Cells

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Microbial fuel cells (MFCs) have demonstrated the capability for achieving efficient and reliable conversion of wastewaters to energy. However, two of the major limitations in achieving large-scale power generation with MFCs to date are the low power output and the usually long start-up time of the system. These are mainly associated with the sluggish bacterial kinetics and inefficient anode material employed for MFCs. We have demonstrated in this study that modification of the anodes with conducting polymers, such as polyaniline (PANi) and polypyrrole (PPy) can be successfully used to address the issues of anode efficiency, as well as to support faster bacterial kinetics at relatively low cost.

In this paper, we will discuss the use of a galvanostatic polymerisation strategy for the formation of highly conductive, uniform and durable polyaniline (PANi) and polypyrrole (PPy) coatings on stainless steel (SS-304) sheet in aqueous media. We will also discuss a detailed study of the electrochemical kinetic behaviour of stainless steel (SS), PANi coated SS and PPy coated SS anodes during bacterial enrichment of MFCs. In particular, we will demonstrate that the anode kinetics are significantly enhanced by a judicious application of a carefully selected external resistance (R_{ext}). This involves enriching the half-cell reactors under different conditions, including without R_{ext} (Open circuit mode), with $R_{ext}=R_{int}$ (Ohmic region), and with very low R_{ext} (mass transfer region). We will also discuss the extensive use of FTIR and other surface/advanced analytical techniques for characterization of the anodes.

ENZYME-FREE IMPEDIMETRIC GLUCOSE SENSOR BASED ON GOLD NANOPARTICLES/POLYANILINE COMPOSITE FILM

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ABSTRACT

A non-enzymatic impedimetric glucose sensor was fabricated based on the adsorption of gold nanoparticles (GNPs) onto conductive polyaniline (PANI)-modified glassy carbon electrode (GCE). The modified electrode (GCE/PANI/GNPs) was characterized by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The determination of glucose concentration was based on the measurement of EIS with the mediation of electron transfer by ferricyanide ($[Fe(CN)_6]^{3-}$). The $[Fe(CN)_6]^{3-}$ is reduced to ferrocyanide ($[Fe(CN)_6]^{4-}$), which in turn is oxidized at GCE/PANI/GNPs. An increase in the glucose concentration results in an increase in the diffusion current density of the $[Fe(CN)_6]^{4-}$ oxidation, which corresponds to a decrease in the faradaic charge transfer resistance (R_{ct}). A wide linear concentration range from 0.3 to 10 mM with a lower detection limit of 0.1 mM for glucose was obtained. The proposed sensor shows high sensitivity, good reproducibility, and stability. In addition, the sensor exhibits no interference from common interfering substances such as ascorbic acid, acetaminophen, and uric acid.

STUDIES ON ETHNOMEDICINAL PLANTS OF NAGALAND AND PHYTOCHEMICAL ANALYSIS OF *PRUNUS PERSICA*

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Nagaland has a rich reservoir of traditional knowledge on medicinal plants. As part of a collaborative research partnership with Indigenous people of Chungtia village in Nagaland, we documented firsthand ethnobotanical information on 135 Nagaland plants still in current use as medicines (Kichu *et al.* 2015). This highlighted 7 plants used for skin related ailments of likely microbial origin that had not been previously studied for their antimicrobial properties or bioactive constituents relevant to their traditional use. Screening of the 7 plants identified roots of *Prunus persica* as having the strongest antimicrobial activity. Partitioning of the ethanolic root extract between *n*-hexane, DCM, EtOAc and water and chromatographic purification resulted in two compounds from the EtOAc partition: *ent*-epiafzelechin-(2α→O→7',4α→8')-(-)-*ent*-afzelechin (active against *S. aureus*, *E. coli*, *P. aeruginosa* and *S. typhimurium*) and afzelechin (no antimicrobial activity detected against strains tested) and three compounds from *n*-hexane partition: α-cyanobenzyl benzoate (active against *S. aureus*, MRSA, MDRSA, antibiotic sensitive *E.coli* as well as *P. aeruginosa*), β-sitosterol and stigmast-4-en-3-one (both active against *S. aureus*, MRSA, MDRSA, antibiotic susceptible *E. coli* and *S. typhimurium*). This is the first report of *ent*-epiafzelechin-(2α→O→7',4α→8')-(-)-*ent*-afzelechin and α-cyanobenzyl benzoate possessing antibacterial activity. This presentation will describe the background of this research project and isolation and structure elucidation studies for *P. persica,* an important medicinal plant of Chungtia village.

Kichu, M., T. Malewska, K. Akter, I. Imchen, D. Harrington, J. Kohen, S. R. Vemulpad and J. F. Jamie (2015). "An Ethnobotanical Study of Medicinal Plants of Chungtia Village, Nagaland, India." *Journal of Ethnopharmacology* **166**: 5-17.

Exchange Coupling between the 4f-electrons and the π-Radical of the $[LnPc_2]^0$ Molecular Nanomagnets

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We investigate the intra-molecular exchange coupling mechanism within $[Ln^{III}Pc_2]^0$ (Ln^{III}=Tb^{III}, Dy^{III}, Ho^{III}, and Er^{III}) between the 4f-electrons in Ln^{III} and the spin-1/2 radical in the phthalocyanine (Pc) ligands. A series of *ab initio* multi-configurational Complete/Restricted Active Space Self-Consistent-Field (CASSCF/RASSCF) calculations were performed for a number of spin states of the $[Ln^{III}Pc_2]^0$ molecules, followed by diagonalization of spin-orbit coupling (SOC) on the basis of the optimized multi-configurational states (RASSI), using Molcas 8.0 code. In CASSCF calculations where only seven lanthanide 4f orbitals and the singly occupied π radical orbital are included, the exchange coupling is constrained to be ferromagnetic by symmetry, and the calculations show that the magnitude of the ferromagnetic exchange decreases with the number of unpaired electrons in the ground Hund's rule Russell-Saunders term. Inclusion of additional π-π* excitations via RASSCF shows that an anti-ferromagnetic mechanism is triggered by spin polarization, whose contribution also decreases with decreasing number of the unpaired 4f-electrons.

We developed a model Hamiltonian to describe the exchange coupling between Ln^{III} 4f-electrons and the Pc_2 radical, accounting for the two dominant microscopic ferromagnetic and anti-ferromagnetic mechanisms resulting in the calculated exchange coupling energy splittings.

Expanding antibiotic chemical space through precursor-directed biosynthesis

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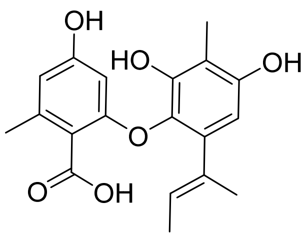
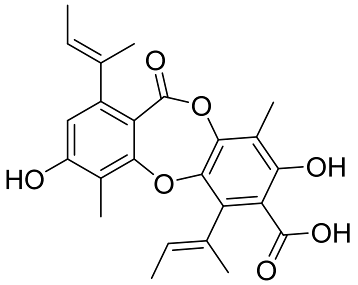
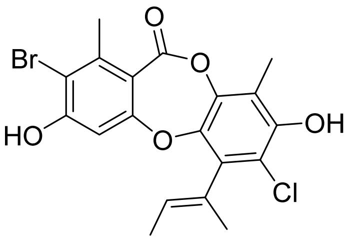
Nidulin is a fungal depsidone antibiotic first isolated in 1944 from the fungus *Aspergillus nidulans*. Nidulin shows potent antibacterial activity against methicillin-resistant *Staphylococcus aureus* (MRSA). In this study, we have employed a combination of natural products chemistry, precursor-directed biosynthesis and chemical derivatisation to expand chemical space around the nidulin pharmacophore. Initial optimisation of culture media led to two new fungal metabolites, 7-carboxyfolipastatin and unguinolic acid, as well as four previously reported compounds. In precursor-directed biosynthesis experiments, *Aspergillus unguis* was supplemented with halide salts, leading to three new depsides, unguidepside A, unguidepside B and 5-bromoagonodepside B, and one new depsidone, 2-bromo-7-chlorounguinol. Finally, a semi-synthetic approach was employed to generate six nidulin analogues. All natural, unnatural and semi-synthetic compounds were screened for antibacterial, antifungal and cell cytotoxicity activities. Based on these bioassay results, a structure-activity relationship for the nidulin pharmacophore was proposed.



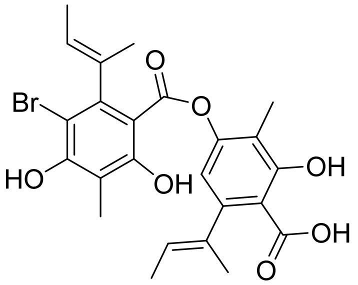
unguinolic acid



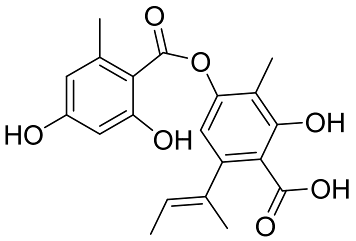
7-carboxyfolipastatin



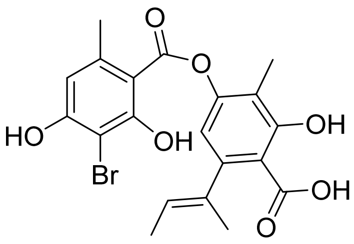
2-bromo-7-chlorounguinol



5-bromoagonodepside B



unguidepside A



unguidepside B

EXPLOITING METAL IMPURITIES IN CARBON NANOTUBES FOR THE DIRECT SYNTHESIS OF ELECTOACTIVE MATERIALS

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Among its many applications, carbon nanotubes (CNTs) have undoubtedly proven itself to be an important and versatile material for electrochemical energy conversion and storage in the 21st century. While the role of CNTs as a substrate for electrocatalysts, as well as their direct usage as catalysts for energy conversion and storage is well documented, there are still many uncertainties regarding the origins of their electrochemical activity. This can be ascribed to the metal impurities that arise inevitably from their synthesis procedures. Recent investigations have demonstrated that these metal impurities can play a significant role in influencing the electrochemical activity of CNTs (1). This study attempts to exploit these metal impurities and use them for the direct synthesis of carbon-based electrochemical catalysts for water splitting. Insights obtained from this investigation will provide another piece of the puzzle that surrounds the role of impurities in CNTs and the part they play in the origin of the electrochemical activity that arises from CNTs.

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EXTENSIVELY REARRANGED CYTOTOXIC NORDITERPENES FROM THE AUSTRALIAN NUDIBRANCH *GONIOBRANCHUS SPLENDIDUS*

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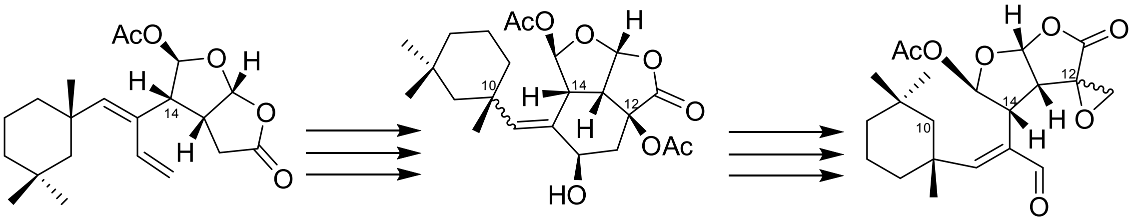
An individual *Goniobranchus splendidus* specimen collected from Mackay, Australia, was found to contain an array of secondary metabolites sequestered from the nudibranchs dietary sponge. From a total extract of 17.5 mg, fifteen known terpenes including four spongian diterpenes, eight rearranged oxygenated diterpenes, and three rearranged oxygenated norditerpenes were isolated.[1]

In addition, two oxygenated norditerpenes possessing unprecedented carbon skeletons have been characterized from the conspicuously patterned mollusk. Their relative configurations were investigated by spectroscopic analyses at 700 MHz informed by molecular modelling and DFT calculations. A biosynthesis from spongionellin[2] is proposed and provides insight into the stereochemistry of epoxygoinolide-1 and goniolide. Epoxygoniolide-1 was moderately cytotoxic to selected cancer cells: its biological profile is currently under investigation.



Spongionellin

Goniolide

Epoxygoniolide-1

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Facile synthesis of rGO nanocomposites with TiO_2 and ZnO for water oxidation

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Efforts have been made to improve the performance of ZnO and TiO_2 in several applications, such as photocatalysis and electrochemical devices. The combination of these oxides with other components including noble metals, doping and inclusion of carbon materials can result in high performance in their activities. Reduced graphene oxide (rGO), a two-dimensional environment of carbon atoms, exhibits novel electronic properties such as zero band gap and fast electron transport. We prepared pure ZnO, TiO_2 and rGO-ZnO, rGO-TiO_2 nanocomposites using microwave-hydrothermal method. All diffraction peaks are consistent with the wurtzite ZnO structure, and anatase structure of TiO_2. The FEG-SEM images of composites presented regular particles distributed on the rGO sheets for rGO-ZnO nanocomposites, while images of rGO-TiO_2 nanocomposites reveled irregular shapes. All Raman analysis for the nanocomposites presented two prominent bands around 1366 cm^{-1} (D band) and 1593 cm^{-1} (G band) assigned to the defects within the hexagonal graphitic structures and phonon vibration of sp^2 bonded carbon atoms in graphene sheets, respectively. FTIR spectra of materials revealed that the bands assigned to organic groups situated at the edges of GO sheets are missing from the FTIR spectra for both nanocomposites, which indicate the reduction of GO. Cyclic voltammetric studies of rGO-ZnO showed that samples have sufficient oxidizing power for water oxidation. The reduced graphene oxide affects the structural characteristics of ZnO, as well as the electrochemical properties. The resulting nanocomposites exhibited electronic interaction between ZnO and rGO sheets, which improved the electrocatalytic oxidation of water.

Facile Synthesis of Spirooxindolyl Isoxazoline *N*-Oxides via [1+4] Annulation Mode

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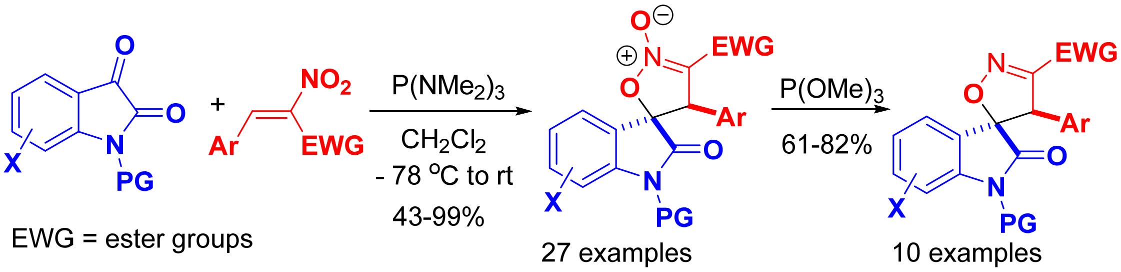
Recently, the classical Kukhtin-Ramirez adducts, which are readily generated from trivalent phosphorus reagents and 1,2-dicarbonyl compounds, have proven to be rich in organic reactivity through their dipolar oxyphosphonium enolate species.[1] Typically they undergo a variety of organic synthetic reactions acting as carbene surrogates or 1,1-dipoles.[1] In 2015, our group reported a $P(NMe_2)_3$-mediated reductive [1+4] annulation of isatins with enones, leading to facile and efficient synthesis of spirooxindole-dihydrofurans.[2] Presumably this reaction proceeds via Kukhtin-Ramirez zwitterions as the key active intermediate. Accordingly it unveils a simple and efficient protocol to construct five-membered carbo- and heterocycles through the [1+4] annulation mode. Most recently, Ashfeld group has developed formal [1+4] cycloaddition of 1,2-dicarbonyls and *o*-quinone methides by the same strategy.[3] As part of our continuous efforts to develop new annulation reactions, herein we present a new $P(NMe_2)_3$-mediated reductive [1+4] annulation of isatins with nitroalkenes, leading to facile syntheses of spirooxindolyl isoxazoline *N*-oxides and spirooxindolyl isoxazolines.



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Facilely Synthesized Dual-emissive Carbon Dots for Ratiometric Detection Al^{3+} ions

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ABSTRACT

Carbon dots (CDs) have widely attracted scientist's interests due to their extraordinary optical/electric properties, including a high PL quantum yield (QY), biocompatibility and environmental friendliness. Therefore, CDs have been successfully employed in a series of applications, such as PL-based sensing. However, most of previous reports are based on the following two situations. (i) The reported CDs-based sensing systems were established on the basis of PL quenching response. (ii) Only single emissive CDs with short or long emission wavelength could be successfully prepared and employed in sensing systems. Herein, we present a green and facile approach to obtain dual-emission CDs from ascorbic acid by hydrothermal treatment for the one time, which avoids the request of tedious synthetic methodology or the use of expensive/toxic solvents and starting materials.

The sensor CDs-based exhibits the dual-emissions peaked at 410 and 535 nm, respectively, under a single excitation wavelength of 355 nm. The emissions of 535 nm can be selectively enhanced by Al^{3+} ions, while the blue PL as an internal reference is not affected. The detection limit of this ratiometric probe is as low as 1.19 μM, which is lower than the defined limit (7.4 μM) by World Health Organization (W.H.O.). Because of the facile synthesis, attractive PL properties, and environment friendly, the dual-emissive ratiometric PL sensor could be extended to the application in the biological, chemical and environmental fields.

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Factors on machine learning performance for chemical databases

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Abstract

Machine learning methods are growing fast and their applications are anticipated to solve intractable problems in many areas. Usually, the performance of machine learning models is affected by many complicated factors. The accuracy and redundancy are two basic features of input descriptors and have been considered directly impacting on model performances. In regression modeling for chemical databases, how they affect models is not that straightforward. To explore these two factors on regression for chemical databases, four machine learning models are built with various input accuracies and redundancies. The results suggest that the accuracy effects on regression models are roughly related to the correlation with the target value of the dataset. If the correlation value becomes larger due to descriptor accuracies improved, the possibility of obtaining more accurate prediction is better than that with low accuracies. No tendentious effects of the descriptor redundancy on the performance of the regression model for these chemical databases are disclosed. This indicates the redundancy is an uncertain factor, which may be unnecessary to intentionally avoid in chemical database modeling.

Fe (III) – the Third Generation Catalyst for Regioselective Protection of Diols

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ABSTRACT

Regioselective protection plays a very important role in organic synthesis, espicially in carbohydrate chemistry, for the construction of carbohydrate building blocks that are used as donors or acceptors in complex oligosaccharide synthesis.[1] Stoichiometric amounts of organotin reagents had been most widely used in selective protection[2] due to the high regioselectivities obtained, coupled with relatively straightforward manipulation, which uses have to be limited or banned now due to their inherent potential toxicity. The reduced amounts of organotin reagent as the first generation catalyst[3] and an organoboron reagent (Taylor's catalyst) as the second generation catalyst[4] have been successfully used for the selective protection of carbohydrates recently, however only showing good selectivity for vicinal *cis*-diols. In the most recent, we reported an Fe(III)-based catalyst which led to high regioselectivities with very broad substrate scope in the alkylation of diols and polyols.[5] The present experiments showed that Fe(III)-based catalyst was also a good catalyst for the regioselective acylation of diols and polyols (Fifure 1). Fe(III) reagent as the third generation catalyst has a great potential to be widely used in regioselective protection considering that iron is not only of low cost and high abundance but is also non-toxic and generally environmentally benign.

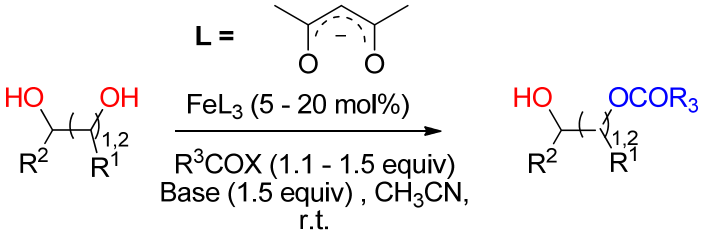

Figure 1. Fe (III)-catalyzed regioselective acylation of diols

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Fermentation of over-ripe bananas using a new microbe, *Pseudomonas mendocina*.

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This paper reports the production of ethanol by fermentation of three varieties of over-ripe bananas, using three different immobilized microbes. One of the three microbes used was a novel bacterium isolated from sugarcane syrup and was identified as *Pseudomonas mendocina* Strain RS_001. The other two microbes used were the common *Saccharomyces cerevisiae* and *Aspergillus niger*. The microbes were immobilised on coconut tree leaf sheath.

The best yield of ethanol 17.7±1.0% (v/v) was obtained with synergism of the novel bacterium and *Saccharomyces cerevisiae*, over three days of fermentation, using the banana variety referred to as *Seeni* in Sri Lanka. It is a very common *Musa* species and is available in abundance.

Three types of wines were developed from the banana belonging to the *Musa* species called *Embul* in Sri Lanka. The quality of these wines compared well with commercially available wines and had better antioxidant activities.

Production of bio-ethanol from over-ripe bananas is cost effective and it is suitable for tropical countries, which lack optimum conditions for grape cultivation. The product development of wines and the production of bio-ethanol from over-ripe bananas could lead to a sustainable bio-fuel industry in Sri Lanka, as well as being a good solution for postharvest losses and solid waste management of over-ripe bananas.

Producing bio ethanol from over-ripe banana is eco-friendly and cost effective. The main objectives of this research were bio ethanol production using three varieties of over-ripe bananas and product development of bio-fuel and alcoholic beverage using several microorganisms.

FIRST-PRINCIPLES STUDY OF ADSORPTION OF LITHIUM POLYSULFIDES ON 3D POROUS GRAPHENE

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Lithium-sulfur (Li-S) battery has revolutionized the energy storage arena due to its high theoretical energy density, which is 5 times greater than Li-ion battery, non-toxic nature and the high abundance of sulfur in nature. However, due to the fact that the entire mechanism is governed by a complex chemistry where the anode, electrolyte and the cathode interact with each other, several issues have prevented the practical applications of Li-S batteries so far. One of the key issues is the dissolution of intermediate lithium polysulfides (LiPSs) in the organic electrolyte leading to deposition of Li_2S_2/Li_2S at the anode surface. An effective way to supress the polysulfide shuttle and achieve long cycling life is to confine LiPSs within a three-dimensional (3D) porous graphene structure. In this study, first-principles density functional theory is employed to understand the ability of 3D porous graphene to retain LiPSs inside its porous framework. The interaction between LiPSs and graphene surfaces has been systematically investigated including electronic structure, binding strength and charge transfer. We have gained insight into how porous graphene influence the adsorption of long chain LiPS in terms of van der Waals interaction and chemical bonding.

FLOW SYNTHESIS, CHEMOSELECTIVE AND STEREOSELECTIVE HYDROGENATION OF NORCANTHARIDIN INSPIRED SCAFFOLDS

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After recent publication of an extensive SAR library of norcantharidin inspired tetrahydroepoxyisoindole carboxamides, several highly-functionalised scaffolds having potent cytotoxic properties (≈ GI_{50} to Cisplatin) were reported (Spare, 2017). This study saw to develop a more efficient synthesis of the Ugi Intramolecular Diels-Alder (IMDA) reaction using flow methods. Optimisation saw a significant increase in the yield and purity compared to the analogous batch reaction (Wright, 2002). These products were then subjected to an array of flow hydrogenation conditions, which once optimised, saw the successful chemoselective reduction of a single olefin bond. Upon further optimisation, the second olefin bond was chemoselectively reduced with the ability to control the conformation of the newly formed stereocentre.

Stereoselectivity was achieved through use of different catalysts in the hydrogenation process. 10% Pd/Al_2O_3 achieved reduction with the stereochemistry favouring the thermodynamically favoured product, CH_3 *trans* to the oxo bridgehead. However, the use of 5% Pt/C-sulphided at low temperatures gave a preference for the CH_3 *cis* to the oxo bridgehead, the kinetically favoured product. Likely due to the electrostatic interaction/repulsion of the large sulphur moiety of the catalyst with the oxo bridgehead, allowing different directionality of hydrogenation, thus determining the final position of the CH_3 group. Further this was applied to three analogues of this scaffold with all products conforming to the observed trend.

Fluorescence decay pathways sensitive to circularly polarised excitation

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Understanding polarization decay processes in photo-excited states of conjugated systems is crucial towards optimizing the operation of a wide range of devices, such as organic light emitting diodes and ultrafast polarization switches. Here, we demonstrate the existence of different decay pathways for circularly polarised excitations in the supramolecular aggregates of a *chiral* conjugated polymer poly [9,9-bis[(S)-2,6-dimethylhexyl]-2,7-fluorene-alt-benzothiadiazole] by using Fluorescence detected Circular Dichroism (FDCD). FDCD is a highly sensitive technique that measures differential emission intensity when excited with left and right circularly polarised light allowing for insight into the polarisation dependence on fluorescence. We find that the emission characteristics arising from intramolecular charge transfer and excitonic energy states are different and likely influenced by the local environment. We attribute these differences to arise from polarization sensitive non-radiative decay.

Fluorescent sensing arrays to measure complex environments

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The development of analytical tools to identify and quantify chemical species in complex fluids is of interest to many, from environmental scientists to forensic investigators to biological researchers. Fluorescent sensing offers the sensitivity required for such studies. To date, the majority of studies aimed to develop fluorescent tools have focussed on the development of selective fluorescent sensors, in which a probe is designed to be highly selective and specific for an individual analyte. However, many such studies fail to screen all possible interferents, whether structurally-similar analytes, proteins, or competing ligands. For the study of analytes in complex solutions in which spatial resolution is not required (such as environmental waterways, or blood serum), fluorescent sensing arrays are proving to be valuable. Such systems involve the use of multiple fluorescent sensors which are cross-reactive with a set of analytes. Rather than a selective response to a single analyte, the set of probes gives a characteristic "fingerprint" response to each analyte.

We are developing novel strategies to generate fluorescent sensing arrays. For example, we have adopted a library-screening similar to that employed in drug-discovery to reduce a library of fifty-five thiophene-containing molecules to a set of four that can distinguish metal ions. We have also developed an assay containing a single probe in different solvents. These general strategies will have impact on the breadth of analytes that can be sensed in complex solutions in the future.

FLUORSCENTLY LABELLED PEPTIDES THAT BIND TO THE COMPLEMENT C5A RECEPTOR

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ABSTRACT

C5a is a complement system peptide, which plays an important role in pro-inflammatory mediation following its activation. Many inflammatory disorders such as rheumatoid arthritis and inflammatory bowel disease have been associated with elevated C5a levels. PMX53 is a potent cyclic-peptide mimetic antagonist, which acts at C5a receptors in a competitive manner and is widely used to study interactions at the C5a receptor. Despite the compound having progressed to human clinical trials, the molecular mechanism is still not well understood and the compound is not detectable in plasma. In order to characterise its interactions at a molecular level, effective bioluminescent tools need to be developed.

We will report here on the synthesis of PMX53 and a structurally related peptide agonist neighbour (YSFKPMPLaR) with fluorescent and lanthanide-based probes such as europium using a range of spacer-groups between the peptide and the dye. These peptide-dyes provide us with an effective mean to detect signalling. Future work on these bioluminescent ligands, will then focus on functional assays, namely cAMP assays and calcium assays to characterise these molecules interactions and downstream signalling effects. Ultimately, this should allow us to measure the residence time of PMX53 via competition-association binding assays. The results of this work are expected to provide us with vital insight into the characterisation of receptor-ligand interactions of PMX53 at the C5a receptor.

Fragment-based development of diaryl ethers as inhibitors of *Ec*DsbA

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The rapid development of bacterial resistance to current antibiotics and limited number of novel compounds in the antibiotic drug pipeline threatens to send the 21st century into a post antibiotic era.[1] Antivirulence agents which do not kill or inhibit bacterial growth, but inhibit the ability to cause an infection have been hypothesised to exert less selective pressure for the development of resistance.[2] One potential antivirulence target is DsbA, a dithiol-disulfide oxidoreducease enzyme that catalyses the formation of disulfide bonds in newly synthesised proteins that are located in the periplasm.[3] Multiple studies with bacteria lacking a functional DsbA have been shown to have attenuated virulence and reduced capacity to cause infection.[4]

Biophysical screening has previously been employed to identify several fragments that bind to *Ec*DsbA.[2] Here we present the structure-aided fragment-based design of inhibitors of EcDsbA based on a diaryl ether core identified by fragment screening. Exploration of multiple vectors around the core as well as the use of biophysical assays to assess solubility and binding/affinity with *Ec*DsbA are demonstrated along with structural data of complexes of compounds bound to the protein.

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Free Radical Carbonylation of Arenes Mediated by Visible-Light Photoredox Catalysis

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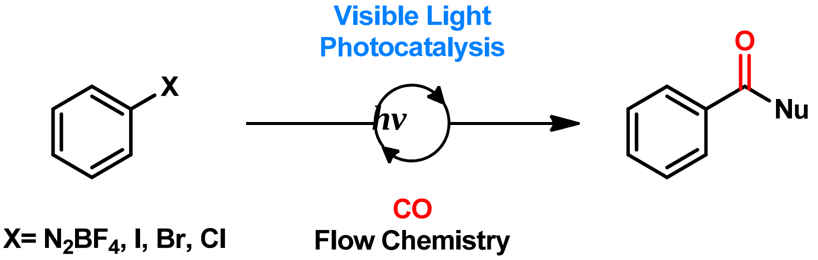
Palladium-catalysed alkoxy- and aminocarbonylation of aryl and alkyl (pseudo)halides provides convenient access to aromatic esters and amides. The broad application of this approach has been restricted by functional group tolerance, high reaction temperatures and moderate catalyst efficiency and turnover. In contrast, free radical carbonylation has been developed to address the limitations of palladium-catalysed transformations.[1] The free radical carbonylation of aryl and alkyl (pseudo)halides is limited by the challenges associated with the generation of carbon-centred radicals under benign conditions.

Visible-light photoredox catalysis has emerged as a method to generate carboncentred radicals under mild reaction conditions.[2-3] As part of our interest in developing mild methods for catalytic carbonylation, we have developed a visiblelight photoredox reaction for the carbonylation of aryl and alkyl substrates. This presentation will detail our recent work in the alkoxy- and aminocarbonylation of aryl radical precursors using continuous flow technology.



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Full-crystalline Hierarchical Monolithic Zeolites as Superiorly Active and Long-lived Catalysts

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Zeolite catalyst played an important role in converting methanol and/or olefins into higher valued chemicals with great market demand. However, the present zeolite catalysts often suffer from slow diffusions of reactants/products in narrow micro-channels, leading to low effectiveness and even quick deactivation. For the obvious diffusivity advance and the resulted improved catalytic performance, hierarchical zeolites have drawn more and more attentions in recent years. Actually, to satisfy necessary mechanical strength requirement in industrial applications, developing high-performance hierarchical zeolite catalyst must based on monolithic bodies rather than only the zeolite powder. However, academic studies from the view of fundamental research were widely neglected in this field.

Herein, by re-crystallizing the shaped binder/zeolite body with assistance of controlled organic template steam, full-crystalline monolithic hierarchical zeolites were prepared. Obvious intra-crystalline mesopores were *in-situ* created while maintaining high mechanical strength in re-crystallization. A remarkable advantage of mass transfer and utilization factor was revealed in such hierarchical monolith, which means more acid sites will be accessible after re-crystallization. Due to the improvement of diffusivity, hierarchical full-zeolitic monolithic catalyst demonstrated higher propylene yield and slower deactivation rate in C4 olefin cracking (OCC) and methanol-to-propylene (MTP) reaction. Moreover, highly prolonged cycle time, which was more than 2000 h and three times as long as that of commercial catalyst, was realized in catalysing MTP under industrial condition. Such catalyst as well as its OCC and MTP process has been successfully applied in industry with advantage of high space velocity, good stability and low energy consumption.

Gas Adsorption in Mg-Porphyrin-based Porous Organic Frameworks: a Computational Simulation

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ABSTRACT TEXT

A novel type of porous organic frameworks, based on Mg-porphyrin, with diamond-like topology, named POF-Mgs was computationally designed, and the gas uptakes of CO_2, H_2, N_2, and H_2O in POF-Mgs were investigated by Grand canonical Monte Carlo simulations based on first-principles derived force fields (FF). The FF, which describe the interactions between POF-Mgs and gases, were fitted by dispersion corrected double-hybrid density functional theory, B2PLYP-D3. The good agreement between the obtained FF and the first-principle energies data confirmed the reliability of the FF. The results indicate that under proper conditions, [1, 2]POF-Mg are potential candidates for H_2 purification. Furthermore our simulation shows that the presence of a small amount of H_2O ($\leq$ 0.01 kPa) does not much affect the adsorption quantity of CO_2, but the presence of higher partial pressure of H_2O ($\geq$ 0.1 kPa) lead to the CO_2 adsorption decrease significantly. The good performance of POF-Mgs in the simulations inspires us to design novel porous materials experimentally for gas adsorption and purification.

Electronic and Vibrational Spectroscopy of Nicotine in the Gas-Phase

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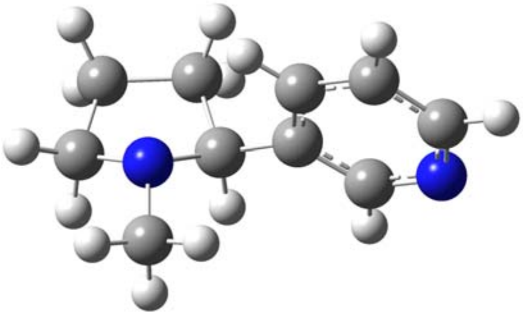
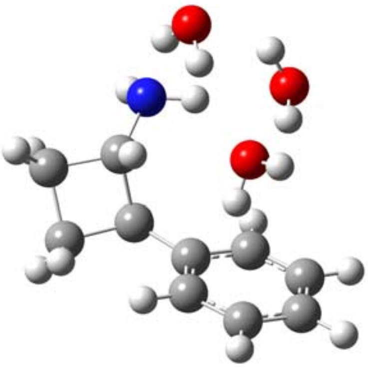
The pharmacological activity of neurotransmitter molecules such as nicotine is contingent on that molecules ability to bind to the appropriate receptor. This binding is contingent upon molecular geometry, or conformation. The gas-phase electronic spectrum of nicotine, and neurotransmitter analogue 2-phenylcyclobutaneamine have been recorded by two-colour R2PI spectroscopy. Based on theoretical calculations, and experimentally recorded IR-UV ion depletion infrared spectrum, a conformational assignments have been made. Water clusters of both species have been observed and structural assignments have been made.





Genetic Algorithm-based Automatic DFTB Repulsive Potential Parameterization for Solid and Molecular Compounds

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DFT-tight binding (DF-TB) is a fast approximation to DFT that uses a 2nd order expansion of the Kohn-Sham total energy equation with respect to charge density fluctuation. DFTB can provide an efficient approach for large solid and molecular systems compared to DFT, which requires much more computational resources. The total energy of DF-TB consists of a band structure term, a Coulombic interaction term, and a repulsive potential; the first two terms are already available for many elements whereas the repulsive potentials for most elemental pairs are not. This presentation will showcase an automated genetic algorithm-based DF-TB repulsive potential parameterization scheme that generates a fitting series for any given elements and optimizes the corresponding repulsive potentials. The preliminary benchmarking of systems such as ligated gold clusters (e.g. $Au_9(PPh_3)_8^{3+}$) and PH_3-Au(111) system shows that the parameterization scheme can produce repulsive potentials for both solid and molecular compounds. We also benchmarked our automatic generated repulsive potentials for P-C-H-O systems against 3ob and mio parameters and showed comparable structural optimization results.

Glucose entrapped in titania under mild environmental conditions

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ABSTRACT

Considerable attention has been paid to Immobilization of enzymes onto inorganic materials for direct electron transfer of metalloproteinsin recent years. The commonly used immobilization methods include physical entrapment, physical adsorption, and covalent coupling. However, these methods usually involve complicated synthetic procedures, which are often carried out under harsh experimental conditions, and with use of toxic and expensive reagents. Hence, under mild environmental conditions, development of efficient immobilization methods, which can achieve a uniform enzyme loading on the solid support, is important and highly desirable. Braun et al first reported the sol-gel encapsulation of biomolecules in 1990. The authors showed that enzymes, trapped within a porous oxide matrix, retain their biological activity. Blin describes direct one-step immobilization of glucose oxide in well-ordered mesostructured silica. There is a maximum loading of GOD, around 11wt%, that can be entrapped in the silica network and the entrapped enzyme maintains its activity. TiO_2, one of inorganic support, has been used to immobilization enzymes since it is biocompatible, chemical and thermal stability. In this work, we report a facile one-step immobilization approach of enzymes mesoporous TiO_2 by the unique combination of glucose oxidase, catalase and titanium precursor and subsequent aging for one week. This approach is based on our recent work on the synthesis of Protein-Mediated Synthesis of Nanostructured Titania. This is the first demonstration of an in vivo method for CGC immobilization onto inorganic materials TiO_2. The CGC shows fast direct electrochemistry.

Gold mobilisation in the environment: the role of *Chromobacterium violaceum*

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The processes/drivers for gold mobilisation from primary ore bodies to secondary ore deposits are not well understood. The bacterium *Chromobacterium violaceum*, naturally present in soils and waters in sub-tropical regions, is known to roughen ultra-flat gold surfaces (Fairbrother, 2009), but their role in mobilisation is not well understood. This research examines the dissolution and speciation of gold in the presence of *Chromobacterium violaceum.* This was achieved by monitoring the formation of dissolved gold complexes when gold foil (Au(0)) is stored over time in the presence of the bacterium. Analysis was achieved using High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry (HPLC-ICPMS). Results indicate the formation of a gold cyanide complex $[Au(CN)_2]^-$ in solution. This research increases our understanding of the role of *Chromobacterium violaceum* in the mobilisation of gold in the environment.

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GRAPHENE/POLY (BRILLIANT CRESYL BLUE)- MODIFIED ELECTRODE FOR DETECTION OF NITRITE

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ABSTRACT

A selective and highly sensitive electrochemical method, based on a reduced graphene oxide/poly(brilliant cresyl blue) composite film-modified glassy carbon electrode, was developed for the determination nitrite. The composite film was prepared by electrochemical reduction of graphene oxide and electrochemical polymerization of brilliant cresyl blue, respectively. The modified electrode was characterized by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The electrocatalytic activity of modified electrode toward the oxidation of nitrite was studied by cyclic voltammetry and amperometry. Cyclic voltammograms showed that nitrite undergoes irreversible oxidation at 0.77 V at modified electrode which is 0.30 V less than that of bare GCE. This shows the efficient electrocatalytic activity of the composite film. The electroanalytical application of the composite film was done by amperometric technique. The film shows a response time of less than 1 s and wide linear range of detection from 1.0 μM to 2.0 mM. The developed sensor was successfully examined for real sample analysis with tap water and it showed a stable and reliable recovery data with high reproducibility. Experimental results showed that the proposed electrode could be used as an effective and sensitive sensor for the determination of nitrite.

GROWTH OF MESENCHYMAL STEM CELLS ON A FREEZE-GELATED CHITOSAN-PECTIN SCAFFOLD

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ABSTRACT

Cartilage and bone related injuries are both costly to treat. In addition, current methods of treatment, such as autologous grafts, are limited by the inherent differences in mechanical properties they possess when compared to the original cartilage or bone. For this study, a scaffold for potential tissue engineering applications was made from chitosan and pectin, both natural polymers. These polymers are reported to be biocompatible and viable for use as a platform for cell proliferation and implantation. The scaffold was fabricated using freeze-gelation, which is a more efficient method than most methods in use today. The scaffold was characterized, and shown to have a porous morphology and to be thermally stable.

The scaffold's potential for tissue engineering was tested using human bone marrow-derived mesenchymal stem cells, which have the potential to differentiate into either cartilage or bone. An MTT cell activity assay showed the scaffold was not cytotoxic, and supported the proliferation of the mesenchymal stem cells, which is the first step towards tissue engineering for cartilage and bone.

HEPARAN SULFATE MIMETIC POLYMERS WITH ACTIVITY AGAINST DENGUE VIRUS

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The sulfated glycosaminoglycan heparan sulfate (HS) is ubiquitous on the surface of all mammalian cells and is utilized as an entry receptor or co-receptor by many viruses e.g., HIV, enterovirus 71, respiratory syncytial virus, human parainfluenza virus, HSV, Dengue and so on. Blocking the interactions of viruses with cell surface HS using HS-mimetics is a promising therapeutic strategy against viral infections. A library of 50 anionic homopolymers and copolymers were synthesized as HS mimetics to investigate their activity against different viruses. All HS mimetics were produced by RAFT polymerization in aqueous media. The polymers were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC), which indicated low polydispersity. Additionally, to confirm the structure of these mimetics, monomer reactivity ratios were determined at low monomer conversion following diverse linear least-squares methods including Finemann-Ross (FR), inverted Finemann-Ross and Kelen-Tudos (KT) methods. The monomer reactivity ratios, calculated from all methods, indicated formation of random copolymers during polymerization. The activity of these synthetic HS mimetics was evaluated against Dengue virus. Amongst the library, compounds were identified that significantly reduced the plaque formation in a plaque reduction neutralizing test (PRNT). The library will also be tested against a range of other viruses that utilize HS.

Highly Luminescent and Stable Lyotropic Liquid Crystals based on Europium β–Diketonate Complex and Ionic Liquids

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The soft lanthanide luminescent materials are impressive for their tunable and self-assembling characters, which facilitate them to be an attractive emerging materials field of research. For this aim, the novel luminescent lyotropic liquid crystals (LLC) with different mesophases have been fabricated by ionic liquids (IL) based europium β–diketonate complexes and an amphiphilic block copolymer (P123). The ILs were used both as the solvent and also as the linkage for stabilizing the doped complexes. The analyses by XRD and FTIR revealed convincingly that the IL cations had established an effective connection with both the β–diketonate ligand and the EO blocks of P123 *via* strong hydrogen bonding interactions. Therefore, an extremely long decay time of the excited state was obtained in complex and an excellent photostability of such luminescent LLCs could be achieved. Their long-period ordered structures had been investigated by small-angle X-ray scattering measurements and the better luminescence performance was found in the most organized mesophase. Noteworthy, the LLCs could yield an effective confining effect on the europium complex accompanied by a sizeable elongation of the excited-state lifetime and an enhancement of the energy transfer efficiency, reaching a remarkably high value. More importantly, the modulated luminescence properties observed in different mesophase structures would offer the potential and powerful possibility to allow these unique composite LLCs present for fabricating soft luminescent materials with tunable functions.

We are thankful for the financial supports from the National Natural Science Foundation of China (21373127 and 21673129).

High-Performance Yne-Diyne Bridged Organic Dyes for Dye-Sensitized Solar Cells

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Our previous research indicated that power conversion efficiency of dye-sensitized solar cells (DSSCs) can be significantly improved by introducing a diyne unit in dye molecules. In order to further improve the light harvest ability, two novel organic dyes coded as **FSD104** and **FSD105** were synthesized by replacing the single-bond-bridge between electron donor (triphenylamine) and π-linker (anthracene) with triple-bond-bridge to obtain an extended conjugation. These two dyes were fully characterized by ^{1}H NMR, ^{13}C NMR and HRMS, etc. The photophysical and electrochemical properties and photovoltaic parameters of DSSCs sensitized by these two dyes were well investigated. The adoption of the triple-bond-bridge effectively reduces the energy gap of the dyes and broadly extends the adsorption spectra, resulting in a remarkable increase of power conversion efficiency. The results show that **FSD105** with cyanoacrylic acid group has a remarkably higher electron lifetime in the TiO_2 conduction band and greater dye-loading amount on TiO_2 than the other dyes, which guaranteed a higher short-circuit photocurrent density and open circuit voltage. Thus, the cell based on **FSD105** shows the highest power conversion efficiency of 4.14%. These results demonstrate that dyes containing a diyne unit always exhibit excellent performance and the power conversion efficiency could be further improved by extending conjugation.

This work was supported by the Natural Science Foundation of Jiangsu Province (BK20140780).

Hit-to-lead optimisation: single agents for the treatment of Chagas disease

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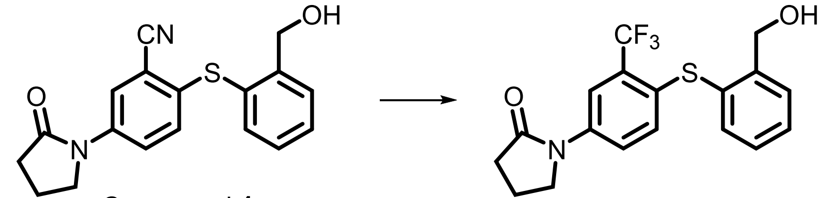
ABSTRACT:

In 2014, GSK performed a high-throughput-screen of 1.8 million compounds against three kinetoplastid parasites. This data was published as an open source in an effort to encourage research and drug development for these neglected diseases.(1) A simple arylthioether compound (compound **1**) was found to have desirable activity against *Trypanosoma cruzi* (the parasite responsible for Chagas disease) and was selected as the hit compound for this project. The initial investigation led to the discovery of an even more potent compound, with a superior pIC_{50} of 7.5 (compound **2**).



Compound **1**
pIC_{50} - 6.6

Compound **2**
pIC_{50} - 7.5

This class of compounds showed promising results in acute in vivo efficacy studies However, several issues have been identified for this chemical series, such as toxicity and low exposure. A full toxicity study was undertaken and several alerts were identified that relate to CNS and cardiovascular toxicity. In order to address these concerns, future analogues have been focused to decrease toxicity and increase exposure. This will be achieved by exploring lipophilicity, solubility and increasing microsomal stability.

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Hollow Fe_3O_4 as nanoelectrocatalyst for molecule catalysis toward electrochemical immunoassay

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ABSTRACT

In this work, we prepared hollow magnetic iron oxide nanoflowers (Fe_3O_4HNFs) as nanoelectrocatalyst to obtain a multi-functionalized redox signal tag for high-performance thionine (Thi) catalysis toward ultrasensitive protein detection. Briefly, Au-Thi-Au with good conductivity and large surface area was prepared to enhance the immobilization amount of redox molecular (Thi). Simultaneously, to improve catalytic efficiency, Au-Thi-Au (redox molecule) was further anchored on the surface of Fe_3O_4HNFs (nanoelectrocatalyst). Obviously, the as-prepared Au-Thi-Au@Fe_3O_4HNFs as signal tag combines the merits of electrochemical activity, catalytic activity, magnetic response as well as nanocarrier, which is employed in electrochemical immunoassay. Importantly, owing to the hollow structure and high activity site of Fe_3O_4HNFs, the signal tag of Au-Thi-Au@Fe_3O_4HNFs exhibits high-performance Thi catalysis even in the absence of substrate, thus, giving a highly sensitive method for electrochemical detection of alpha fetoprotein (AFP) down to the 0.033 pg mL^{-1}. Compared with traditional enzyme-based signal amplification, the proposed immunosensor avoids the addition of any substrate in testing solution, and shows good stability, sensitivity and accuracy.

HYDROGEN SULFIDE GAS SENSING USING COPPER NANOPARTICLE-SENSITIZED POLYANILINE

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Hydrogen sulfide (H_2S) is one of the most common gases generated in livestock and poultry operations. Prolonged exposure to this gas, even at trace concentrations, poses a number of health risks to the surrounding community. Thus, constant monitoring of gas production from these facilities is important. However, the conventional method of detection, usually a pulsed-fluorescence analyzer, demands elaborate procedures and is usually, of high cost. This study aims to investigate the potential of developing chemically synthesized gas sensing materials based on polyaniline (PANI) doped with copper nanoparticles (CuNPs). The composites were synthesized via *in situ* polymerization of the aniline in the presence of copper nanoparticles. The morphological and structural properties of the composites were examined. Results show that the incorporation of CuNPs improved the sensor's performance in terms of sensitivity to the target gas. This may be attributed to the enhanced surface area of the sensing membrane due to the presence CuNPs. The catalytic properties of CuNPs also contributed to the increased sensitivity of PANI to H_2S gas.

Hydrophobically Directed Asymmetric Synthesis of Chiral GABAs with Quaternary Stereogenic Center

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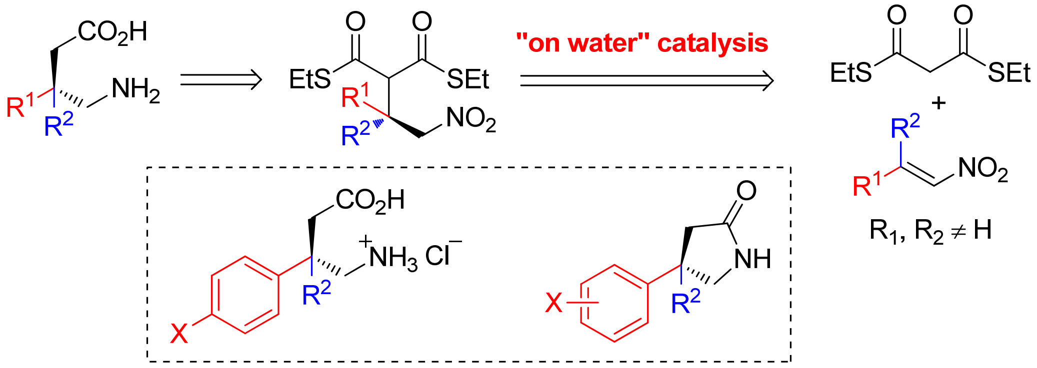
In nature, water is used as reaction enhancer for biosynthetic reactions to sustain life in enzymatic processes, inducing hydrophobic interactions between enzyme and substrates. From the perspective of green chemistry as well as an increased scientific effort to mimic nature, tremendous effort has recently been directed to the development of catalytic reactions in aqueous environments.

In this symposium, we will present our recent discovery that water enables new catalytic reactions for otherwise unreactive substrate systems. Highly enantioselective organocatalytic Michael addition of dithiomalonates to extremely unreactive β,β-disubstituted nitroalkenes, affording both enantiomers of highly enantioenriched Michael adducts with all carbon substituted quaternary centers, has been achieved by employing the "on water condition," which enables enforced hydrophobic interactions between catalysts and substrates due to the hydrophobic hydration effects. The developed "on water" protocol was successfully applied for the scalable one-pot syntheses of chiral GABA analogs with all-carbon quaternary stereogenic centers at the β-position, which might show highly interesting pharmaceutical properties.[1]



β,β-disubstitued chiral GABA analogues

[1] J. H. Sim, C. E. Song, *Angew. Chem. Int. Ed.* **2017**, *56*, 1835.

IMPACT ASSESSMENT OF MATERIAL CORROSION IN WASTE TO ENERGY PLANT

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Typically, municipal solid waste contains large portion of combustible matter to recover heat energy by thermal treatment. Conventional combustion is promising and well-known technology to treat municipal solid waste safely. However, municipal solid waste in Korea consists of miscellaneous materials with incombustible materials and large amounts of moisture, which prevent heat recovery from combusting. Due to fossil fuel limitation, technological development of renewable and sustainable energy such as waste to energy (WtE) is necessary. Solid refused fuel (SRF) mainly consists of combustible matter which is derived from municipal solid waste by separation process, and heat content was maximized by intensive drying process. Combustible matter in SRF contains plastics fraction to increase calorific value. In this study, commercial SRF boiler with 100MW capacity was selected to investigate impact assessment of corrosion issue in boiler tube and convection pass. Usually, chlorine content of fuel occur boiler tube corrosion, and alkali metals such as K, Na, Ca occur slagging and fouling. Based on the fuel analysis, the average chlorine content of SRF was 1.32%. In XRF analysis, the chlorine content in boiler tube ash and bottom ash was 6.1% and 4.3%, respectively. In SEM-EDX analysis, the chlorine content in corrosion part on boiler tube was ranged from 11.95% to 30.52%.

Acknowledgement

This work is supported by Korea Ministry of Environment (MOE) as Knowledge-based Environmental Service (Waste to Energy and Recycling) Human Resource Development Project.

Impact of 2-methylbutanal photochemistry in the atmosphere

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Aldehydes and ketones are major components of oxidized molecules in the atmosphere. The photochemistry of these compounds has a significant contribution in atmospheric chemistry. Norrish Types I and II (NT-I and NT-II) as well as triple fragmentation (TF) are well-known pathways to decompose these molecules.

Despite many years of research on the photochemistry of these molecules, the fundamental photochemical mechanisms of these pathways are still a controversial subject due to their complex nature. In NT-I reaction, the molecule dissociates to the free radicals, HCO and alkyl, on the triplet state. In the NT-II reaction, enol and alkene are formed from a 6-membered ring transition state following a 1-5 hydrogen shift from the carbon centre to the oxygen centre. In the TF reaction, molecule dissociates to H_2, CO and alkene on the S_0 state. In the atmosphere, the fate of products of NT-I, NT-II and TF are different. For instance, the alkene produced form NT-II can participate in ozonolysis reaction and enol is suggested to produce organic acids. In contrast to NT-I reaction, in NT-II, it is not yet well understood that which states, S_0, T_1 or both, are involved in the photolysis mechanism. The triple fragmentation channel contributes to formation of H_2 in the atmosphere.

Our aim is to scrutinize the photochemical mechanism of 2-methylbutanal by investigating wavelength dependent photochemistry of this molecule in the 300 - 330 nm region. Thus, the quantum yields of products are calculated in the photolysis of 2-methylbutanal with FTIR spectroscopy.

Impact of GaN and AlGaN Surface Chemistry on pH response

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AlGaN/GaN-based high electron mobility transistor devices contain a charge-sensitive "2-dimensional electron gas" at the interface between GaN and AlGaN. Modulation of the charge characteristics at the surface of the device affect this electron gas, and by monitoring the electrical response of the device to changes at the surface, the device can be used as a functional chemical sensor. The oxides of both Al and/or Ga on the surface are sensitive to changes in pH. Sensing devices have been constructed and used in a reference-electrode free configuration to detect changes in pH. Interestingly, GaN-capped devices exhibit linear behaviour with respect to pH changes while uncapped devices (with an uppermost AlGaN layer) exhibit a U-shaped response. With careful analysis of the sensor response and accounting for differences in the ionic strength of the solution, we show that the responses are consistent with the expected variation in the amphoteric oxide chemistry of Ga *vs* Al. This interpretation is supported by the results of studies using X-ray photoelectron spectroscopy. This work demonstrates that in a reference electrode-free configuration, a GaN cap on the AlGaN/GaN device is required to achieve the desired linear response to pH.

INSULIN IN MOTION: STRUCTURAL DYNAMICS EFFECTS ON INSULIN-RECEPTOR BINDING

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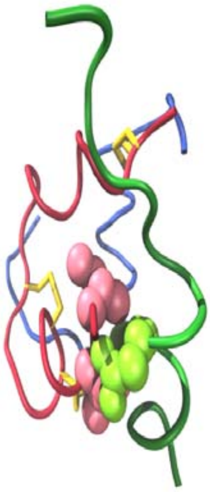
ABSTRACT TEXT

Understanding the molecular conformation that insulin must adopt to bind to the insulin receptor (IR), and the structural changes the hormone must undergo to access this conformation, is critical for elucidating the mechanism of insulin receptor activation and for the intelligent design of improved insulin-based treatments for diabetes. It has long been recognised that the C-terminus of the insulin B chain must move away from body of the hormone for IR binding (A). Here we demonstrate that the N-terminal helix of the A chain must also partially unwind in order to engage with the receptor (B). Molecular dynamics simulations reveal that this unwinding motion is controlled via conformational change of the A6-A11 disulfide of insulin in order to extend or contract the $C\alpha$-$C\alpha$ distance (C). Synthesis and biological testing of insulin analogues where the A6-A11 disulfide has been replaced by either a shorter *cis* carbon-carbon double bond or a longer *trans* C=C linkage, confirm that it is only when the A6-A11 $C\alpha$-$C\alpha$ distance can be contracted to ~4.0 Å, instigating unwinding of the A-chain N-terminal helix, that insulin receptor binding and activation can occur.



Interaction of Glycolipid S-TGA-1 with Bacteriorhodopsin and Its Functional Role

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It has been demonstrated that lipid molecules in biological membranes are responsible for the functionalization and structuration of membrane proteins. However, it is still unclear how the interaction of lipid molecules with membrane proteins is, correlated with the function of the membrane proteins. Here we first developed an evaluation method for the interaction between membrane proteins and lipid molecules via surface plasmon resonance (SPR) analysis. Bacteriorhodopsin (bR), which was obtained by the culture of halobacteria, was used as a membrane protein. We prepared SPR sensor chips covered with self-assembled monolayer containing mercaptocarboxylic acids, and immobilized bR onto them. Then, we evaluated the interactions with various lipids that have different structures. As a result, the halobacterium-specific glycolipid S-TGA-1 was found to have much higher affinity with bRs than other lipids. This is probably due to not only hydrophobic and electrostatic interactions but also hydrogen bonds with sugar moieties in the glycolipid. Next, we analyzed the roles of the lipid in the structuration and functionalization of bR. CD analysis showed that S-TGA-1 could promote trimerization of bR monomers more efficiently than any other lipids. Flash photolysis further indicated that bR trimers formed by S-TGA-1 reproduced the photocyclic activity of bR in purple membrane, halobacterium-membrane. These results suggest that S-TGA-1 promotes trimerization of bR through strong interactions and consequently fulfills the bR's function efficiently.

Intramolecular Tsuji-Trost Reaction; Efficient Access to Mono-Allylated 1,3-Diketones.

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Alkylation of a doubly activated position, such as the 2-position of a 1,3-diketone, has historically been difficult due to di-alkylation at the C-2 atom, C- vs O-alkylation, and instability of alkylating agents to the generally required basic media. This tends to give rise to a mixture of several alkylation products.[1] This has been combatted by utilising one-electron oxidising agents such as ceric ammonium acetate,[2] and beta-diketones in the form of their cobalt(II) complexes [3] to broaden the scope of their C-alkylations, however there are numerous limitations to the current methods.

The development of a simple, efficient, and scalable synthesis of several structurally diverse 2-allyl-1,3-diketones via an intramolecular Tsuji-Trost allylic alkylation reaction is reported. The scope and limitations of the reaction will be discussed, along with its use in the preparation of various natural product scaffolds.

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Introducing Chemistry in Early Childhood

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The periodic table is an icon, as easily recognizable as the Eiffel Tower, Michelangelo’s David and John Howard’s eyebrows. And yet, with its seemingly endless rows of meaningless numbers and symbols, it carries the burden of being dull, complex and strictly nerds only. The development of this reputation can be averted by introducing the periodic table in early childhood. Young children have an unquenchable thirst for knowledge and delaying until high school seems a lost opportunity. The basic characteristics of sixteen elements from the periodic table provided the inspiration for the characters in the two picture story books targeting children 4-7 years. As children read the books they become familiar with the personalities and peculiarities of the characters (who just happen to be elements!) in a learning environment devoid of pressure and expectations. One of the two main characters is the lazy Lord Argon who prefers not to mix with people in town as he believes he is far superior to anyone else. The other is Gallium, the young apprentice metal worker who has a peculiar habit of melting when he gets frightened. Imbedded in the stories and illustrations are further clues about the elements ready to be discovered by children later in primary school. The books can be used as a teacher resource to link in with the current science curriculum and other initiatives already being taught in primary schools.

An investigation into the introduction of gold nanoparticle to a proline-calixarene gel matrix by laser ablation.

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ABSTRACT TEXT

This study was aimed at exploring the stability of gold nanoparticles (AuNPs) in a proline calix[4]arene hydrogel. Various methods of in situ and ex situ gelation were attempted, leading into different morphological characteristics which has been observed by using atomic force microscopy (AFM). The initial investigations were related to the stability of AuNPs in varying concentrations of proline calix[4]arene solution. Interesting effects that are both concentration and time dependent were found to result from laser ablation synthesis in solution (LASiS) of a gold plate in proline calix[4]arene solution. LASiS of gold in warm gel solution appeared to significantly hinder the process of ablation to the point where there is no gold in solution.

Investigating Lawsone Mechanisms For Potential Use In Latent Fingermark Enhancement

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Lawsone is quickly gaining interest in the forensic science community as a potentially new chemical treatment for the development of latent fingermarks, particularly on porous surfaces. Lawsone, or 2-hydroxy-1,4-naphthoquinone, is found in the leaves of the henna plant and has been widely used in hair and skin dyes for thousands of years. It's dying properties are supposedly due to its affinity for the protein, keratin. It has been suggested that lawsone reacts with amino acids in fingermark residues to produce a red or purple/brown colouration capable of revealing fine details of the fingermark. The proposed mechanism for this occurrence (Figure 1) is similar to that of the reaction between amino acids and ninhydrin, a compound already in use for latent fingermark enhancement and structurally similar to lawsone.(Jelly et al. 2008) However, more investigation is needed to confirm how this mechanism occurs, and preliminary experiments reveal that the reaction between lawsone and amino acids is not as simple as first thought. The work presented will discuss current results about how lawsone and amino acids interact with each other, and will look to support or refute the proposed mechanism.

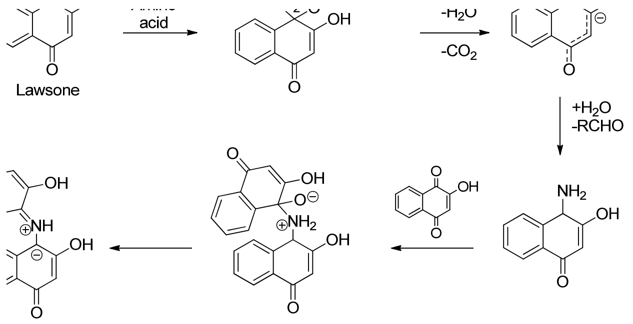

Figure 1: Proposed mechanism of the reaction between lawsone and amino acids (Jelly et al. 2008)

Jelly, R. et al., 2008. Lawsone: a novel reagent for the detection of latent fingermarks on paper surfaces. *Chemical Communications*, (30), p.3513.

INVESTIGATING THE LIGHT INDUCED MOTION OF MICRODROPLETS

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The development of chemical vessels for the controlled movement of materials in fluid environments has the potential to open up new vistas in fluidic platforms for diagnostics, chemical "cargo" transport, targeted drug delivery and multi-droplet information systems.[1] The simplest approach to this, to date, has been the use of liquid droplets whose movement is generally the result of changes in surface tension or Marangoni effects.

In 2015, we reported on the photo-induced movement of a lipophilic droplet as a result of the irradiation of the medium surrounding the droplet.[2] Subsequently, we have developed a simple droplet system that consists of an organic solvent or mixture of solvents containing a photoisomerizable molecule and associated surfactant. When the droplet itself is irradiated with ultraviolet or visible light either on or in aqueous media, it moves towards or away from the direction of irradiation depending on the type of light and photoactive material used. The mechanism of droplet movement is under investigation.

In this paper, we will report on our investigations into this light-induced chemopropulsion of microdroplets using a variety of techniques including ultraviolet/visible, fluorescence, and Raman spectroscopy, as well as contact angle and interfacial tension measurements.

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Investigation into poor Sr recoveries in multi-radionuclide analysis of soil samples

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High chemical recoveries are crucial to quantitative radiochemical analysis of environmental samples. In order to achieve lower detection limits, often required for environmental analysis, sample masses are increased. However, this increases the likelihood that matrix interferences will reduce chemical recoveries.

Our current radiochemical separation method for strontium (Sr) in soils comprises an aqua regia leach, calcium phosphate co-precipitation, extraction chromatography using Eichrom Sr-Spec® resin cartridge, followed by elution of Sr for liquid scintillation analysis (LSA) operated in Cherenkov counting mode.

Poor chemical recoveries for Sr were consistently observed when analysing large mass (>10 g) soil samples. Preliminary investigations suggested up to 80% of losses occurred prior to column loading and further losses of up to 20% during column separation and purification. A comprehensive study was conducted to determine the sources of these losses.

To assess losses that occurred prior to column loading, variables such as major cation and phosphate concentrations both in the sample and added to the process were investigated as well as other co-precipitation techniques. To assess losses during column separation and purification, the Sr-Spec® resin cartridge retention capacity was investigated in the presence of the major elemental concentrations typically found in soil samples.

Results of this investigation will be discussed and conclusions presented.

IRON(III) CHLORIDE-CATALYZED CLAISEN REARRANGEMENT REACTION OF ALLYLOXYARENES UNDER MICROWAVE CONDITIONS

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ABSTRACT

Nowadays, the production of chemicals using the principles of green chemistry is extensively studied regarding to the considerable impact of the environmental problems. The Claisen rearrangement of allyloxyarenes are typically performed in a long reaction time and high temperature range 180-225°C. Recently, the microwave has been demonstrated as a powerful tool for organic syntheses since it can give significant advantages over the conventional heating, *e.g.*, quick reaction, high chemical yield, and high selectivity. Moreover, $FeCl_3$ as Lewis acid is considered as one of desirable catalyst due to its cheapness, easily handle and environmental friendly properties. In this study, the microwave heating effects for the Claisen rearrangement of allyloxyarenes in the presence of $FeCl_3$ catalyst was investigated. This reaction was performed in a test tube by mixing the substrate with $FeCl_3$ catalyst in the various solvents. The mixture was heated at low temperature 80°C. As a result, $FeCl_3$ catalyst was able to initiate the rearrangement at 80°C in a short reaction time. It have been proved using 1-crotyloxynaphthalene that the reactions occur through intramolecular rearrangement not intermolecular one. The microwave heating effects were affected by the kind of solvents. The microwave heating enhanced the reaction of allyloxyarene derivatives in decalin and 1,2-dichloroethane compared with conventional heating. It was suspected that $FeCl_3$ forms a complex with the aromatic ring of allyloxyarenes. The formed complex species was expected to efficiently absorb the microwave, so the reaction would be accelerated. The formation of the iron complex is being investigated through ^{1}H-NMR relaxation time study.

IS THERE A GULF BETWEEN EDUCATION AND INTELLECTUAL PROPERTY?

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The aim of any good intellectual property (IP) system is to encourage innovation, leading to sustainable economic growth. Given the specialist knowledge required to innovate in a technical field such as chemistry, the innovators and creators of the 2020's are likely to be the graduate students of today. Are we preparing these future innovators to sustainably grow the Australian and worldwide economy? Are Australian universities positioned to take advantage of the next wave of innovators?

The authors of this paper have considerable recent experience studying, researching and teaching in Australian universities (MBS) and representing Australian universities regarding IP rights around the world (RDG).

We contend that Australian universities are poor at formally teaching IP rights to science and engineering students at any level, in our experience. Rather, research students absorb knowledge of IP rights by academic osmosis from their supervisors, who themselves may have only limited experience with IP rights, if any. Thus, knowledge gained by students tends to be superficial or situation-specific, rather than a fundamental understanding of patents and patentable inventions. This leads to students and researchers unable to identify if their research may be patentable. This is potentially depriving research institutions of additional income streams.

We explore how educational institutions might be able to implement formal IP teaching programs and what benefits may flow from introducing formal IP education into higher degree programs, in order to better equip tomorrows innovators, and universities, for a more sustainable 2020 and beyond.

ISOINDOLINE NITROXIDE-CONTAINING PORPHYRINS FOR EPR AND FLUORESCENT IMAGING PROBES

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Some porphyrins and their metal complexes play important roles in magnetic resonance imaging (MRI), photodynamic therapy (PDT), anticancer drug and fluorescence imaging because of their preferential selective uptake and retention by the tumors. Recently, spin-labelled porphyrins have received more and more attention as potential molecular magnetic materials and EPR probes in the study of porphyrin excited states. Tetramethyl isoindoline nitroxides can display superior EPR linewidths, compared to other classes of nitroxides.

In this work, isoindoline nitroxide-containing porphyrins were synthesized by the reaction of 5-phenyldipyrromethane and 5-(4'-nitrophenyl)-dipyrromethane with 5-formyl-1,1,3,3-tetramethylisoindolin-2-yloxyl using the Lindsey method. These spin-labeled porphyrins were further characterizated by MS, UV, FT-IR, cyclic voltammetry, electron paramagnetic resonance (EPR), and fluorescence spectroscopy. The electrochemical assay demonstrated that these isoindoline nitroxides-containing porphyrins had similar electrochemical and redox properties as 5-carboxy-1,1,3,3-tetramethylisoindolin-2-yloxyl. The EPR test exhibited these porphyrins possessed the hyperfine splittings and characteristic spectra of isoindoline nitroxides, with typical nitroxide g-values and nitrogen isotropic hyperfine coupling constants. Fluorescence spectroscopy revealed that these porphyrins indicated fluorescence suppression characteristic of nitroxide-fluorophore systems. Moreover, their reduced isoindoline nitroxide-containing porphyrins eliminated the fluorescence suppression and displayed strong fluorescence. Thus these isoindoline nitroxide-containing porphyrins may be considered as the potential probes for fluorescent and EPR spectroscopy.

This work was supported by the National Natural Science Foundation of China (Grant No. 51373128), Key National Research and Development Program (2016YFB1101302), Wuhan Science and Technology Innovation Team of Hi-tech Industrial Project, Hubei Province (Grant No. 2015070504020217), and Innovation Fund for post-graduate education (CX2016004, CX2016012), Wuhan Institute of Technology, China.

Layered Double Oxide Nanocrystals for Ultrafast Removal of Toxic Pollutants

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Heavy metal ions existing in natural underground water and drinking water are causing environmental issues and global health concerns. Especially, arsenic [As(V)] and chromium [Cr(VI)] are hazardous pollutants, which will pose serious risks to human health, living organism, and the ecological system. Herein, flowerlike Mg/Fe layered double hydroxide (MF-LDH) nanocrystals were prepared by a simple hydrothermal method for removal of As(V) and Cr(VI) from contaminated water. After thermal treatment of MF-LDH nanocrystals, the MF-LDH was converted into their corresponding oxide, Mg/Fe layered double oxide (MF-LDO), which maintained the flowerlike structure. The crystal structure, morphology, microstructure and chemical structure were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy mapping, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy. The MF-LDO nanocrystals showed superb removal efficiency for both As(V) and Cr(VI), which showing over 97% removal within 5 min and providing maximum removal capacities of 178.5 mg/g [As(VI)] and 129.7 mg/g [Cr(VI)]. In addition, Au nanoparticles were successfully introduced in the MF-LDO nanocrystals and the products exhibited excellent catalytic conversion rate for reduction of 4-nitrophenol into 4-aminophenol (100% conversion in 5 min). This work provides simple, convenient and cost effective strategies to develop promising materials for water pollutant removal.

LC-MS/MS FOR NEURAL CATECHOLAMINES, DRUGS AND TSPO LIGANDS IN API4000

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Neural catecholamines - dopamine, epinephrine, and norepinephrine - play a unique role in the brain. It acts in the synaptic transmitter metabolism modes of action in psychotropic drugs (Moore and Bloom, 1978). Most studies analyze some neural catecholamines only, and without measuring some related drugs, which affects these catecholamines present in the brain. In this, we have improvised a method to quantify the related drugs, catecholamines, metabolites, and (translocator protein) TSPO ligands for our future studies. In this study, we have optimized a single liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis using an API4000 mass spectrometer to achieve simultaneous measurement of neural catecholamines, related metabolites 3-MT, L-DOPA and Tyr, haloperidol, raclopride, and TSPO ligands PK11195 and FEPPA. The optimizations include comparison of various analytical conditions in a C18 peek column using acetonitrile and H_2O (with 0.1% HCOOH) as the solvent gradient.

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Li-Metal Battery Reactions: DFT Modelling of Ethylammonium Tetrafluoroborate on Li(001)

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ABSTRACT

Society has become heavily reliant on batteries for powering many of our technological devices, however, a number of improvements need to be made in order to make them safer and more durable. During cycling, rechargeable batteries with Li-metal anodes can form large Li-dendrites in the presence of common organic electrolytes. This can lead to short circuiting and inefficiency in charge cycling [1]. Room temperature ionic liquids (IL), used as an alternative to organic electrolytes, have shown promise in improving battery cyclability [2], suppressing catastrophic dendrite formation [3]. This suppression was attributed to the formation of a solid electrolyte interphase (SEI) layer. An understanding of the reaction-mechanisms that form the SEI is therefore crucial.

Using density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations, the reaction of the IL cation-anion pair, ethylammonium tetrafluoroborate [EtNH$_3^+$][BF$_4^-$], on the Li(001) surface was conducted to determine how the IL electrolyte reacts with the Li-metal electrode surface. Thirteen different orientations of [EtNH$_3^+$][BF$_4^-$] adsorbed on the Li(001) surface were found, having binding energies between -1.80 eV to -1.00 eV. Stronger interactions occurred when the anion and the polar amine group of the cation was located closer to the surface. The cation and anion both underwent reduction after reacting with the surface, and there was a tendency for one to three Li-surface atoms to show depletion in their electron density after adsorption of the IL. Using AIMD simulations, the IL was found to be stable and did not dissociate on the surface at room temperature.

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Linear carbon linkage stabilzed by donor-acceptor ligands

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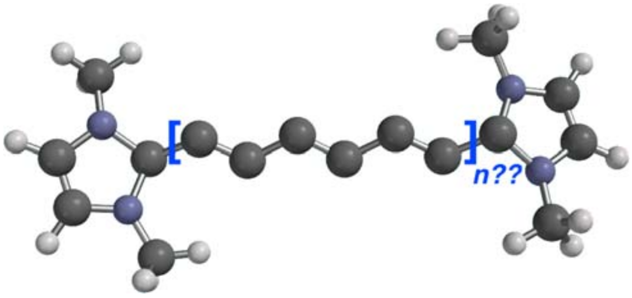
Recent synthetic and theoretical reports of ligand stabilised main group species in donor-acceptor framework further extends the number and range of $L \rightarrow E_n \leftarrow L$ molecules.[1,2] Here we present results of a theoretical study investigating ligand-stabilised C_n moieties. The C_1 and C_2 species have been studied extensively, with a recent synthesis of C_2 stabilised by two donor ligands. Interestingly, synthetic isolation was achievable with the cAAC ligand, but not the NHC ligand.[3] Previously, Bestmann *et al.* (1989)[4] had hypothesised that the ligand stabilisation of C_n units with odd values of n could only be achieved by two donor molecules, but even numbers of n required one donor and one acceptor ligand. The recent synthesis of cAAC stabilised C_2 appears as a contradiction to Bestmann's hypothesis. Subsequently, it is of interest to test Bestmann's hypothesis for longer-carbon chains, and whether they can be stabilised by donor and/or acceptor ligands, and moreover, how long a carbon chain can be until linearity is disrupted? We will report results from our computational investigation, including molecular orbital (MO), natural bond orbital (NBO) and bond dissociation energy (BDE) analysis, to probe the fundamental nature of bonding, thermodynamic stability and electronic structure of these novel C_n systems.



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Long-lived ground state vibrational coherences in phycocyanin-645 at room temperature

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Following the unexpected observation of long-lived oscillations in photosynthetic aggregates, the scientific community has undertaken a significant experimental and theoretical effort. Among the model approaches, several studies tried to explain the origin of the oscillations and the role they may play in mediating the energy transfers processes. Some suggested that correlated fluctuations of the chromophores might or might not be responsible for the long-lived coherent superposition of states, others indicate that vibrational modes resonant with the energy splitting of two excitonic states can lead to efficient quantum energy transfer. On the experimental side, multiple ultra-fast techniques have been used to address the photo-dynamics of a wide range of photosynthetic complexes ranging from reaction centres to light-harvesting complexes. Recently, multidimensional spectroscopy using narrow-band ultra-short pulses allowed to selectively excite few pathways of interest, specifically the ones involving quantum-coherent superposition of different molecular states.

In this study we apply a four-wave mixing technique with pulses characterized by narrow and non-overlapped bandwidths to explore the energy-transfer dynamics within the light-harvesting complex phycocyanin-645 (PC645) from cryptophyte algae. While long-lived coherences were previously reported in this system at cryogenic temperature, here we show that PC645 displays analogous photo-dynamics at physiological temperature. This clearly suggests that vibrational coherences in the ground excitonic state, scarcely affected by the temperature-dependent incoherent bath scattering, are dominant in the investigated photo-excitation regime with high laser intensity. Using computational modeling combined with experimental results, we confirm that the observed coherences are due to the pathways occur in ground excitonic manifold.

Luminescent Iridium(III) Markers For Biological Imaging

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Luminescent metal complexes of ruthenium(II), rhenium(I), iridium(III), gold(I) and platinum(II) show specific properties that are ideal for cellular imaging applications.[1,2] In particular, phosphorescent cyclometalated iridium(III) compounds are proving to be exceptional systems for the development of novel molecular probes for optical imaging in live cells. In fact, the chemical, photophysical and biological targeting properties of these complexes can be readily modulated by altering the coordinating ligands and by coupling to appropriate biological vectors.[3,4] In the last few years, we have been interested in the development of a library of differently functionalised-tetrazolato iridium(III) complexes, aiming to modulate the cellular localisation and cytotoxicity of these probes within a series of living cells lines as well as preserved tissues. We have synthesised complexes with both small functional groups or functionalised with long fatty acid chains to increase their biocompatibility and uptake. The systematic change approach has provided new information on the link between the structure of molecular complexes and their target specificity, yielding at the development of superior diagnostic markers.

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Lung Cancer Diagnosis via Electrochemical Strategy: From miRNA to lncRNA

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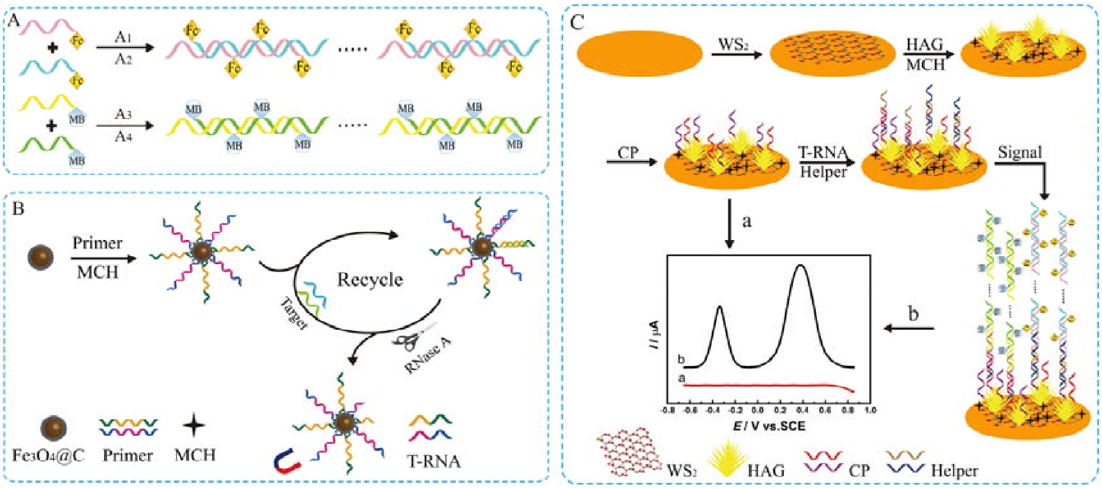
Lung cancer is a global health problem for its incidence, prevalence and high mortality rate. Therefore, sensitive and specific profiling of cancer-specific miRNAs or lncRNAs is significant. Until now, there are only a very few reports about lncRNAs detection using electrochemical biosensors. Therefore, the development of sensitive electrochemical detection of lncRNAs is highly desirable.

During these two years, we have fabricated three novel types of electrochemical genesensors for the detection of lung cancer related miRNAs and lncRNAs biomarkers. First, miR-21 levels were quantified as low as attomolar sensitivity by a target-triggered triple isothermal cascade amplification (3TICA) strategy with the coupling of target recycling, nicking-replication reaction and DNAzyme catalysis. Second, an H19 lncRNA electrochemical biosensor was fabricated based on a three-dimensional ordered macroporous (3DOM) graphene-AuNPs composite active interface and $Ru(NH_3)_6^{3+}$ attached AuNPs@PS signal reporter. Third, a multiplexed biosensor was prepared for the simultaneous detection of two different specific sequences deduced from MEG 3, on the basis of a 3D graphene-like WS_2 interface. In the presence of target specific sequence, an RNase A-aided target recycling amplification was triggered. Fc and (or) MB labelled chain reaction would subsequently generate signal enhancement, which was distinguished at different potentials. The application of these genesensors in real serum samples have also been studied, and the satisfactory results have already obtained compared with the clinical assays.



Scheme 1. Schematic illustration of multiplexed and amplified electrochemical detection of two different specific sequences deduced from MEG 3.

MACROPOROUS HYDROGELS COMPOSED ENTIRELY OF SYNTHETIC POLYPEPTIDES: BIOCOMPATIBLE AND ENZYME BIODEGRADABLE 3D CELLULAR SCAFFOLDS

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Synthetic polypeptides are a class of bio-inspired polymers with well demonstrated biocompatibility, enzyme biodegradability and cell adhesive properties, making them promising materials for the preparation of macroporous hydrogels as 3D cellular scaffolds. Despite this, synthetic polypeptides have been scarcely utilized in the fabrication of macroporous hydrogels. In all cases, the synthetic polypeptide is only one component of the gel, where crosslinkers and other polymers are incorporated into the final gel structure, potentially altering its intended properties and making it difficult to ascertain the true effect of the synthetic polypeptide on the properties of the gel. Therefore, to effectively study the suitability of synthetic polypeptides as a material for 3D cell culture applications, and to better utilize the beneficial properties owing to these materials, the preparation of macroporous hydrogels composed entirely of synthetic polypeptides is desirable.

Poly(L-glutamic acid) (PLG) and poly(L-lysine) (PLL) were copolymerized into random co-polypeptide polymers (PLG-*r*-PLL). Under cryoconditions, macroporous cryogels were prepared using a single copolymer component through direct EDC/sulfo-NHS zero-length coupling between poly(L-glutamic acid) (PLG) and poly(L-lysine) (PLL) residues of the polymer chain. The resulting three-dimensional macroporous hydrogels were composed entirely of biocompatible and enzyme biodegradable synthetic polypeptides. The resulting macroporous cryogels were found to contain large interconnected pores (≥100 μm) highly suitable for tissue engineering applications. Tuning the relative ratios of the amino acid components could result in cryogels with very different pore structures, swelling and mechanical properties, suitable for developing gels for a range of possible soft tissue engineering applications. These cryogels were shown to be enzymatically biodegradable and demonstrated excellent biocompatibility, cell attachment, and cell proliferation profiles with mammalian fibroblast (NIH-3T3) cells; demonstrating the appeal of these novel cryogels as cell scaffolds.

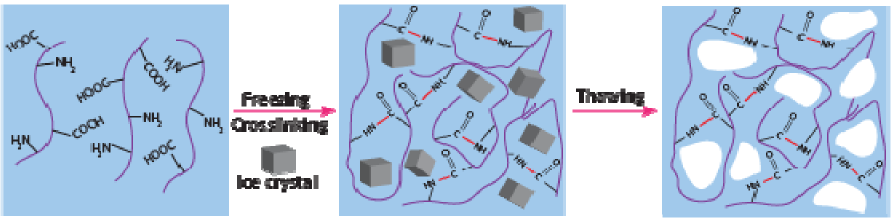

Figure 1: Formation of synthetic polypeptide macroporous cryogels by direct zero-length EDC/NHS crosslinking of a polypeptide copolymer.

Mechanistic Insights on DBU Catalyzed ß-Amination of NBS to Chalcone Driving by Water: Multiple Roles of Water

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ABSTRACT TEXT

DFT calculations were conducted to pursue deeper understandings on the mechanism and the explicit role of trace water in the DBU-catalyzed ß-amination of NBS to chalcone. Being different from previously proposed by Liang et al., a cooperative participation of both DBU and water is noticed in the preferred mechanism. The preferential mechanistic scenario assisted by water undergoes three major steps: the formation of succinimide and HBrO, concerted nucleophilic addition and H-shift, and keto-enol tautomerization. Moreover, we found that DBU-HBrO is unnecessary in the third step and three-water-cluster assisted keto-enol tautomerization is the most advantageous case. It is further noted that the catalytic position of the third water molecule and the proton shift orientation to some extent affect step 3 via O···H−O and O−H···π interactions, which is confirmed by AIM analysis. The computational results suggest that water molecules play pivotal roles as reactant, catalyst, and stabilizer to promote the reaction of chalcone and NBS. The origin of the more stable transition state structure in the rate-determining step of DBU-water catalyzed mechanism is ascribed to noncovalent interactions, halogen bond, and electrostatic interactions than DBU only ones.

Mechanistic studies with NMR on dissolution of cellulose with CO_2

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Cellulose is the most abundant natural organic polymer on earth which can be processed into fibres by wet-spinning. However, cellulose contains an ordered hydrogen bonding network, which makes it insoluble in water and common organic solvents. In commercial processes, the dissolution methods involve toxic CS_2/NaOH/water system, or a greener but expensive N-methylmorpholine oxide (NMMO)/water system. Later, researchers developed more cellulose dissolution media, such as urea/NaOH/water system, ionic liquids and ionic liquid/co-solvent system.

Cellulose was recently reported to be dissolved in DMSO by forming a switchable ionic system with CO_2, which is considered as a green procedure. Here we report our ^{1}H and ^{13}C-NMR studies on cellulose DMSO-*d6* solution obtained using CO_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base. No signal of imine C=N was observed in the ^{1}H-NMR spectrum of DBU, whereas in the ^{1}H-NMR spectrum of the cellulose solution, a broad signal at 8.69 ppm was observed and attributed to C=N***H*** of the $[DBU\text{-}H]^+$ cation. In the ^{13}C-NMR spectrum of DBU, the chemical shift of ***C***=N is 159.57 ppm, whereas the signal of ***C***=NH of $[DBU\text{-}H]^+$ was shifted to 163.00 ppm in the ^{13}C-NMR spectrum of the cellulose solution. In addition, a broad signal was observed at 156.09 ppm, attributing to R-O***C***OO$^-$ anion (R=cellulose), indicating the formation of carbonate anions. These results may suggest that DBU deprotonates the hydroxyl groups of cellulose to form $[DBU\text{-}H]^+$ cations and R-O$^-$ anions which reversibly react with CO_2 to generate R-OCOO$^-$ anions, forming a switchable ionic system and leading to the dissolution of cellulose.

Mechanistic study of the oxa-Pictet-Spengler reaction

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The oxa-Pictet-Spengler (OPS) reaction is an understudied reaction of an arylethanol such as 2-(3,4-dimethoxyphenyl)ethanol **1** and an aldehyde or ketone **2** (Figure 1). The reaction is acid catalysed and assumed to proceed *via* an oxocarbenium ion where cyclisation is through is S_N1-type process but limited evidence has supported this. To date, there are few reports of the enantioselective oxa-Pictet-Spengler reaction,[1] in contrast to the aza-version of this reaction.

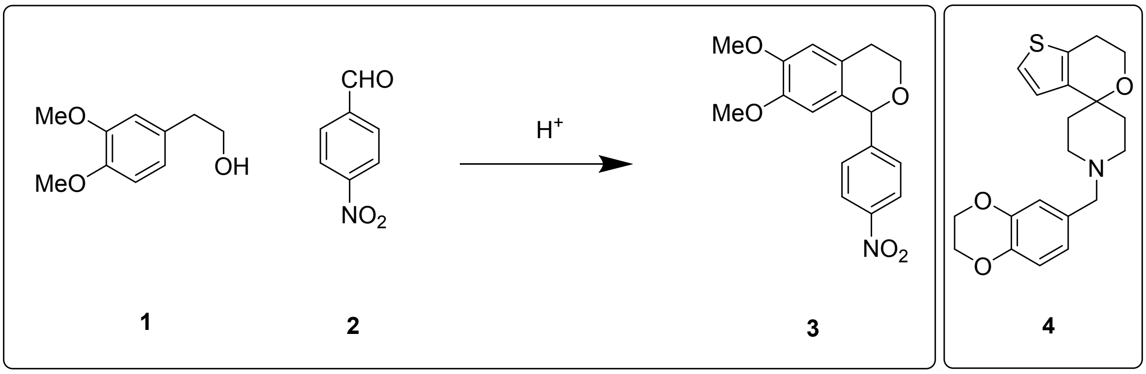

Figure 1. A prototypical oxa-Pictet-Spengler reaction. Solvent, temperature, and catalyst have been evaluated in this work (left). A novel compound made *via* the OPS reaction **4** which showed anti-tubercular activity with a MIC_{90} of 0.063 µM and a CLogP of 3.0 (right).

The OPS reaction is synthetically important because it can produce bioactive compounds such as new drug leads with activity against *Mycobacterium tuberculosis*, the leading cause of tuberculosis.[2]

We have studied the mechanism of the OPS reaction through reactivity patterns, construction of a Hammett plot, and measurement of the secondary deuterium kinetic isotope effects. We present empirical and computational evidence that suggests an S_N2-type process can operate which contrasts with the assumed S_N1-type reaction proceeding *via* the oxocarbenium ion. Implications of our work on the nature of the transition states and hence, the catalysts needed to stabilise them will be described.

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Mesalazine from Salicylic acid: Synthesis involving mild nitration conditions

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Mesalazine (5-aminosalicylic acid) is synthesized from Salicylic acid under mild conditions as compare to reported Mesalazine synthesis. This synthesis includes the regioselective nitration of salicylic acid with of acetic acid/ nitric acid at a lower temperature followed by reduction of nitro group into an amino group. Steps involved (two steps: nitration & reduction) in this synthesis are simple, environment friendly and high yielding. Proposed synthesis of Mesalazine can be used at the industrial level.

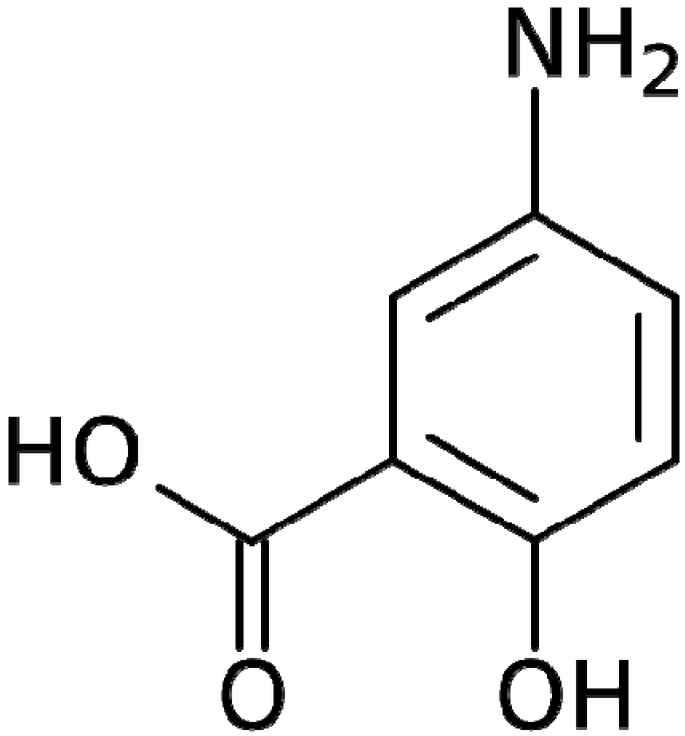

Figure 1: Mesalazine

Metal Complexes of Hemilabile NCN Pincer Ligands in Catalysis

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In search of more efficient catalysts, we have examined the use of hemilabile NCN pincer ligands and transition metal ions as catalysts for a variety of catalysis reactions. The ligand was first investigated to determine the appropriate length of spacer between a central *N*-heterocyclic carbene donor group and two pendant pyrazole arms. As part of this, the coordination chemistry of the ligand was fully explored by complexation to various inorganic salts, resulting in numerous metal complexes, with their structures were elucidated in the solid state. Our group has reported rhodium(I) and iridium(I) complexes of these variable linker ligands were investigated in hydroamination reactions (Messerle 2014). Ruthenium(II) complexes were next investigated as catalysts for transfer hydrogenation (Messerle 2016). Intriguingly, a pentaborate anion was formed during the synthesis of one of these metal complexes, its presence had a remarkable effect on the catalysis. Nickel(II) complexes were obtained and investigated as catalysts for Kumada couplings (Messerle 2017). The NCN pincer ligands also proved amenable to complexation to both gold(I) and gold(III). These gold complexes performed as excellent catalysts for dihydroalkoxylation and intramolecular hydroamination reactions. It was found that complexes containing a longer ethylene linker between the central carbene and pendant pyrazoles resulted in coordinately saturated complexes that are not effective catalysts.

Metal Organic Framework Derived Porous Materials For As (III) Detection

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Prussian Blue (PB) is an often used material for a range of applications, including electrocatalysis and energy, due to its favourable redox properties. Pure PB nanocubes suffer from poor stability under operating conditions for sensing, and as such derivatives of PB such as composites can offer superior performance. In this poster we present a range of PB derived composites and materials, with a primary application of Arsenic sensing. For example, hybrid materials based on FeC_x materials have been developed by simply annealing gold cyanide-Prussian blue composites coated with a tannic acid (AuCN / PB @ KTA) precursor. As (III) sensing on these composites show the addition of Fe_4C and gold contributes to the sensitive response towards arsenic sensing. The effect of electrochemical performances of these composites under different pyrolysis temperatures indicate higher temperature of 650 °C results in a higher sensitivity of 7.30 μA cm^{-2} ppb^{-1} and a LoD of 0.19 ppb for As (III) sensing.

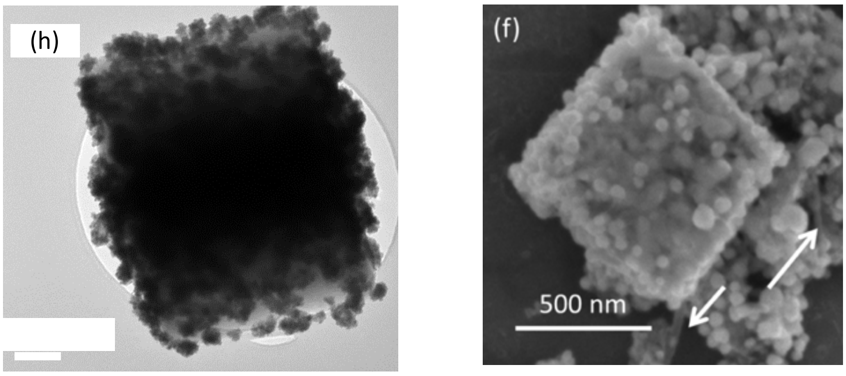

Figure 1 A AuCN / PB composite (left) and a calcined FeCx based composite, both were tested for electrocatalysis or sensing.

MICROWAVE-ASSISTED RING-OPENING COPOLYMERIZATION AND PROPERTY OF POLYCARBONATE

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Recently, the microwave-assisted heating method has become a commonly used and environmentally friendly heating technology in the field of organic and polymeric synthetic chemistry. A series of poly(5,5-dimethyl trimethylene carbonate-co-2-phenyl-5,5-bis(oxymethyl) trimethylene carbonate) (P(DTC-co-PTC)) were synthesized by the microwave-assisted ring-opening polymerization of 5,5-dimethyl trimethylene carbonate (DTC) and 2-phenyl-5,5-bis(oxymethyl) trimethylene carbonate (PTC) using tin (II) 2-ethylhexanoate and aluminum isopropoxide as the catalysts. These co-polycarbonates were further reduced by a palladium-carbon catalyst (Pd/C catalyst, 10%) to make partly deprotected polycarbonates (HPDPC). These two type co-polycarbonates were characterized by gel permeation chromatography, ^{1}H NMR, Fourier transform infrared spectroscopy, UV, differential scanning calorimetry, and automatic contact-angle measurements. The influences of the microwave irradiation time, microwave power, monomer feed molar ratio, different catalysts, and monomer/catalyst feed molar ratio on the molecular weights of copolymers were also investigated. *In vitro* water absorption, degradation and drug release tests indicated that partly deprotected co-polycarbonate HPDPC possessed faster degradation rate, greater hydrophilicity and faster drug release rate than corresponding P(DTC-co-PTC).

This work was supported by the National Natural Science Foundation of China (Grant No. 51373128), Key National Research and Development Program (2016YFB1101302), Wuhan Science and Technology Innovation Team of Hi-tech Industrial Project, Hubei Province (Grant No. 2015070504020217), and Innovation Fund for post-graduate education (CX2016004, CX2016012), Wuhan Institute of Technology, China.

MODIFIED POLYSACCHARIDES AS TEMPLATE FOR THE SYNTHESIS OF POLYANILINE NANOPARTICLES

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Controlled drug delivery systems are used to alter the timing and rate of release of a drug in a specific part of the body. Advances in biotechnology have had a significant impact on the development of stimuli-responsive biomaterials with tunable properties for more controlled and targeted drug delivery. Consequently, the prominent weaknesses of most systems are the cost and time associated with their fabrication. In this study, polyaniline (PANI) nanoparticles were successfully synthesized using cross-linked carboxymethyl chitin (CM-chitin)/carboxymethyl cellulose (CM-cellulose) template, as supported by their spectral and morphological analyses. The template was fabricated by converting chitin and cellulose, extracted from waste materials of squid pens and rice husks, to their respective carboxymethyl derivatives, and their subsequent cross-linking using epichlorohydrin. Release studies, using UV-Vis spectroscopy, showed that there is a sustainable release of indigo carmine by the synthesized materials. PANI nanoparticles offer a promising low-cost drug carrier material.

MOF biosensor for L-Cys without post-modification

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ABSTRACT

L-cysteine (L-Cys) is one of the most important aminoacids. It plays an important role in living systems and in various cosmetic as well as pharmaceutical preparations. Hence, the probing of L-Cys is very significant. Among all detection methods, the electrochemical techniques have been considered as the promising technique owing to the relatively low cost, simplicity, high sensitivity, and selectivity. Metal–organic frameworks (MOFs) as an ideal biosensor candidate for electrochemical reactions have attracted intensive interest because of their advantageous properties, such as their various pore sizes, high surface areas and naked active sites. Herein, We exhibited the application of an heterometal MOF $[Fe^{II}(pz)\ Ni^{II}(CN)_4]$ for the electrochemical detection of L-cysteine without further post-modification.

To investigate the detection of L-Cys, unmodified $[Fe^{II}(pz)\ Ni^{II}(CN)_4]$ was coated on the surface of a gold electrode and cyclic voltammetry measurements was performed in K_2HPO_4–KH_2PO_4 buffer solution (PBS, pH 6.8). After adding the L-Cys into the buffer solution, a new anodic peak appeared at $E_{pa} = 0.895$ V, which can be used as the detected signals for L-Cys. The current density of oxidation peak increased gradually with the increase of L-Cys concentration in the range of 0.10 mM to 1.0 mM. This work provides a new kind of fast and prices sensor for the detection of L-Cys.

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Molecular simulation of DNA triplex structure and thermodynamics

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DNA triplexes are biologically relevant variations on the canonical B-DNA structure, where a triplex-forming oligomer (TFO) binds in the major groove of a duplex. Their formation is known to be associated with the onset of neurodegenerative diseases such as Friedreich's ataxia. Accordingly, the ability to destabilise them, such as through the complexation of minor-groove-binding drug netropsin, has potential therapeutic use. A computational analysis of the structural and thermodynamic changes occurring upon netropsin and/or TFO binding has been undertaken, highlighting the position-dependent effects of netropsin on the major and minor groove widths, as well as the effect of TFO composition (RNA or DNA) on stability. In addition, this presentation discusses the failings of the amber parm99 BSC0 force field in reproducing experimental thermodynamic data for DNA triplexes.

MONOSACCHARIDE TRANSFORMATIONS USING FLOW CHEMISTRY

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ABSTRACT

A number of monosaccharide transformations need prolonged reaction durations, expensive reagents and lengthy purifications. Triflation reactions can take up to 2 hours, require multiple wash steps and most often, a long purification column to isolate products (Best 2010). Triflations involve the reactive trifluoromethanesulfonic anhydride which activates primary and secondary alcohols. The esters synthesised are desirable intermediates however have limited stability at room temperature. Limiting the handling of this reagent and intermediates would be advantageous due to the *in situ* formation of triflic acid. Batch hydrogenations require hydrogen gas handling and pyrophoric palladium catalysts generally using Parr hydrogenators (Hizartzidis 2014). These can take up to 24 hours to go to completion and need to be recharged regularly (Best 2010). These two reactions have been transferred to flow using the Vapoutec R-4® and H-cube®.

We present here novel lactone triflations using the Vapourtec R-4® and hydrogenation of a monosaccharide using the H-cube®. Triflations using flow reactors have been shown to generate benzyne precursors in aryne chemistry (Michel 2014; Yoshida 2014). No reactions have been reported using carbohydrate substrates. There are also few literature examples where flow hydrogenation has been applied to aromatic systems (Hizartzidis 2014). Here we apply for the first time a tandem azide reduction-reductive amination using hydrogenation on a monosaccharide derivative with a flow reactor. We also develop the work on flow triflation using lactone and monosaccharide derivatives.

Multi-functional Persistence Luminescence Nanoparticles for Bioimaging and Therapy

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ABSTRACT

The near-infrared (NIR) emitting Persistent luminescent nanoparticles (PLNPs) are one of the most attractive luminescence nanoparticles for biomedical application, because they have a long afterglow time and no need for *in situ* excitation during the biomedical imaging. PLNPs-based molecular probe not only can completely avoid tissue autofluorescence, light scattering and phototoxicity originating from the excitation source, but also have deeper tissue penetration, due to their emission wavelength located in the NIR window in biological tissue [1]. Herein, we designed a multi-functional PLNPs-based molecular probe for in vivo NIR luminescence imaging and stimuli-responsive chemotherapy. Firstly, a novel composition of NIR emitting PLNPs with superlong afterglow time was synthesised by a citrate sol−gel method. The surface of PLNPs was coated with (3-Aminopropyl)triethoxysilane, and subsequently conjugate to a pH stimuli-responsive Polyacrylic acid (PAA) polymer. The anticancer drug of Doxorubicin (Dox) was loaded into the PAA conjugated PLNPs particles for controlled drug delivery. The PAA functional PLNPs exhibit a bright NIR luminescence and sustained drug release properties.

Reference

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MUTAGENIC ACTIVITY OF THE OXAZOLOPYRIDINE COMPOUNDS: A COMMON SCAFFOLD FOR DRUG DISCOVERY

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Carcinogens cause DNA damage (genotoxicity) which can lead to mutations and cellular transformation due to defective repair of the damage. Oxazolopyridine compounds (OPs) are important molecular scaffolds utilized in many marketed and developing drugs due to their bioactivities. Despite their structural similarity to the known carcinogen, PhIP, potential carcinogenic effects of OPs have not been investigated.

Our lead compound, 2-(3-aminophenyl)-oxazolo[4,5-*b*]pyridine **(1)** was selected as the molecular scaffold of OPs and was found to be non-cytotoxic up to high micromolar concentrations. Interestingly, **1** potently induced DNA damage in a dose dependent manner from low nanomolar concentrations as evidenced by the rapid induction of ɣH2AX foci in HepG2 cells. Using the Ames test, **1** was also found to be mutagenic with a need for prior bio-activation. Compound **1** also significantly increased colony volume of HepG2 cells in a soft agar invasion assay, indicative of strong cellular transformation potential. Despite the lack of cytotoxicity and normal DNA repair kinetics, **1** increases cellular transformation by a currently unknown mechanism. Therefore, analogues of **1** with the deletion of key functional groups were synthesised to determine a structure-activity relationship (SAR). Our data suggests that the oxazolopyridine core of **1** is likely responsible for the observed effects. The formation of an N-oxide at the pyridine nitrogen of the oxazolopyridine core upon metabolic oxidation is likely responsible for the mutagenic effects.

In conclusion, oxazolopyridines demonstrate the hallmarks of a mutagen, likely due to the formation of an N-oxide upon cellular bio-activation.

Nanoengineering hierarchically porous heterogeneous catalysts

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The quest for sustainable technologies to meet the food, energy and material challenges of this century is a key driver for the design of next-generation catalysts and industrial chemical processes. Chemoselective oxidations and hydrogenations of alcohols and carbonyls respectively, and (base)acid catalysed (trans)esterifications, are important reactions that underpin the synthesis of diverse chemical intermediates, and will play a key role in the valorisation of biomass for the production of biofuels and bio-derived chemicals. However, current heterogeneous catalysts are poorly suited to the chemical transformation of bulky reactants, such as lignocellulosic components or oleochemicals from plants or algae, or rapid molecular transport of reactants/products to and from in-pore catalytically active sites. New synthetic methodologies are therefore required to improve the accessibility and connectivity of porous catalyst architectures.

Here we highlight how advances in materials synthesis, specifically the combination of soft- and hard templating methodologies, afford the rational design of hierarchically ordered macroporous-mesoporous architectures of metal oxides with tunable pore dimensions and connectivity. Subsequent functionalisation by metal nanoparticles, organic acids or conformal (acidic, basic or photoactive) oxide monolayers, creates high activity catalysts with enhanced mass transport and active site accessibility for the sustainable production of biofuels and chemical intermediates for the polymer, fragrance, flavourings and pharmaceutical sectors.

Nano-particle based microarray for facilitated phenotypic screening of natural product library in mammalian cells

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ABSTRACT TEXT

Traditional small molecule microarray (SMM) is not applicable for cell-based high-throughput screens (HTS). Although people has used different strategies to achieve cell phenotypic HTS, there are still many limitations, such as not controllable release, extra-chemical synthesis or limited to certain type of chemical reactions for immobilization. Mesoporous silica nanoparticles (MSNs), which has large pore size and high drug loading capacity, has been widely used in drug delivery. Herein, we report the first time the combination of microarray with MSN, to achieve controllable releasing of more than 100 member of natural product, which facilitated phenotypic HTS with several cancer cell lines by varies types of detection methods. The further application of Si-RNA BRCA1 or PARP1 knockdown combined with our MSN-natural product has identified some natural product which has synergetic effect with BRCA1 or PARP1 knockdown. Subsequent cell-based assay has confirmed our finding. This application has demonstrated our strategy has universal application in phenotypic based high-throughput drug discovery.

Nanosized ZSM-5 isomorphously substituted by Ga and aromatization performance

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ABSTRACT TEXT

Modification with isomorphous substitution by Ga can tune the acidity and porosity properties of the ZSM-5 zeolites. In this work, the Ga isomorphously substituted nanosized ZSM-5 zeolite samples GaNZ5-1 and GaNZ5-2 with various Ga content were prepared by post-treatment method in the $(NH_4)_3GaF_6$ solution with different concentrations, and the catalytic properties were evaluated in 1-hexene aromatization.

After the incorporation of Ga atom, the amount of strong Lewis acid sites as well as the total ones increased along with the increasing Ga content, the amount of strong Brønsted acid sites decreased and the weak one increased, which can be ascribed to the formation of extra-framework GaO^+ species contributing to strong Lewis acid sites and the insertion of Ga into the framework of zeolites, forming new weak Brønsted acid sites. Moreover, the lower B/L ratio beneficial for the aromatization was obtained. In addition, the decreasing in microporosity and enhancement in mesoporosity put down to the blockage of micropore by extraframework oxide metal species and the damage due to the acidic medium. An increasing in aromatics yield with the enhancement of Ga content was reached, and GaNZ5-2 achieved the highest aromatics yield of 58 wt.% which can be attribute to the synergistic effect of milder Brønsted and stronger Lewis acid sites.

Natural Products for Drug Discovery in Bangladesh

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Many people in Bangladesh are suffering from different types of diseases such as diabetic, cancer, malaria, leishmaniasis, dengu, dyslipidemia, hypertension, leprosy, cardiovascular diseases (CVDs) etc. Malaria and leishmaniasis are prevalent in the hilly areas of the country. People living there cannot afford to have proper drugs for the treatment of many diseases including malaria and leishmaniasis. Diabetes is prevalent in the whole country and the number of patients is increasing day by day due to rapid urbanization and change of life style. Indigenous people are using plant materials for remedy of these ailments as modern drugs are expensive and unavailable for them. As part of our on-going research on natural products, a large number of plant extracts from Bangladesh origin were screened on normal and streptozotocin induced Type I (IDDM) & Type II (NIDDM) diabetic model rats. Extracts of *Crataeva religiosa, Murray koenigie, Momordica charantia, Zizyphus rugosa, Zizyphus oenoplia, Scoparia dulcis* and *Coccinia indica* showed significant efficacy on different animal. From the active extract of these plants, several secondary metabolites were isolated. Endophytic fungi were isolated from medicinal plants of *Terminila chebula* Retz, *Ocimum basilicum* L, *O. sanctum* L., *Aquilaria malaccensis* Lamk and *Magnifera indica* L., and several novel and known compounds were isolated. The parent extracts and isolated compounds of the fungal strains were tested for antibacterial, antioxidant and cytotoxicity assay against human cancer cells. Secalonic acid A and secalonic acid D showed significant cytotoxicity against human pancreatic cells with IC_{50} values of 7.3 and 1.6 μM, respectively.

Near-Infrared Luminescence Detection of Fingermarks using Coated Exfoliated Egyptian Blue

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Latent fingermark detection using powdering techniques has been carried out for over a century to establish connections between individuals and objects found at crime scenes. Several commercially available powders exhibit luminescence in the visible region of the electromagnetic spectrum, which to some extent can negate the interferences exhibited by dark, multicoloured or patterned substrates. However, there remain many fluorescent, highly patterned and/or reflective surfaces that continue to prove troublesome.

An alternative is to use dusting powders that exhibit near-infrared (NIR) luminescence. As very few substrates luminesce in the NIR region of the spectrum, such powders can highlight ridge detail while avoiding interference caused by inherent background luminescence. We have recently shown that the ancient pigment Egyptian blue can be used as a dusting powder to detect latent fingermarks [1]

Here we present a cetrimonium bromide coated exfoliated Egyptian blue powder for the detection of latent fingermarks. Particle size and surface coating were characterized using scanning electron and atomic force microscopy, dynamic light scattering, and infrared spectroscopy. The luminescence properties of the modified powder were investigated with luminescence spectroscopy, and found not to change significantly compared to the unmodified pigment. The modified fingermark dusting powder gives improved performance for the detection of aged fingermarks with low moisture and oily components on non-porous multicoloured and patterned substrates, compared to uncoated Egyptian blue and commercially visible light fluorescent (Blitz Red) and near-infrared luminescent (fpNatural1) powders.

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New Aspects of Phosphane and Carbene Ligands in Gold Catalysis

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Ligands always have been a key element in gold catalysis.[1] Both gold(I)[2,3] and gold(III)[4,5] catalysts have extensively been applied. For gold(I) both phosphanes and *N*-heterocyclic darbene ligands complexes dominated, for gold(III) mainly *N*,*N*-, *N*,*O*-ligands and *N*-heterocyclic carbene ligands as well as simple halogen anions represent the most important classes of ligands.

We report latest results showing that the phosphane ligands not always remain unreactive. Furthermore, the synthesis of different functionalized NHC ligands and new chiral NHC ligands will be presented. This will include detailed structural studies and first synthetic applications.

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New Bafilomycins Produced by a *Streptomyces* sp. Isolated from a Marine Sponge *Theonella* sp.

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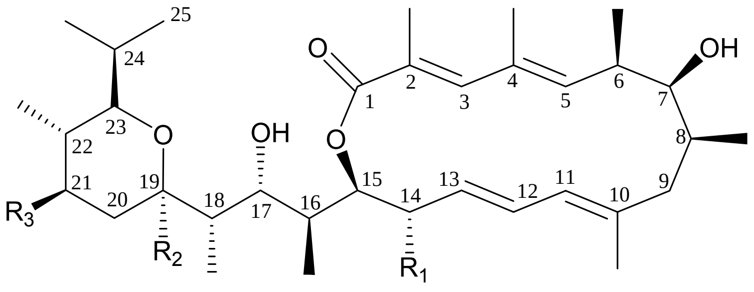
ABSTRACT

Three new 16-membered diene macrolides, bafilomycin M (**1**), N (**2**) and O (**3**), along with two known compounds JBIR-100 (**4**) and bafilomycin K (**5**) and were produced from *Streptomyces* sp. GIC10-1. This bacterium was isolated from a marine sponge *Theonella* sp. The structures of **1-5** were established by spectroscopic methods and by comparison the spectral data with known analogues. These five compounds were found to exhibit significant cytotoxicity toward MOLT-4, K-562, SUPT-1 and LNCaP tumor cells.

Theonells sp.

Streptomyces sp.
GIC10-1



Bafilomycin M (**1**):$R_1=R_2=OCH_3$, $R_3=OH$
Bafilomycin N (**2**):$R_1=CH_3$, $R_2=OH$, $R_3=OC(O)\underset{H}{C}=\overset{H}{C}C(O)OH$
Bafilomycin O (**3**):$R_1=CH_3$, $R_2=R_3=OH$
JBIR-100 (**4**):$R_1=OCH_3$, $R_2=OH$, $R_3=OC(O)\underset{H}{C}=\overset{H}{C}C(O)OH$
Bafilomycin K (**5**):$R_1=OCH_3$, $R_2=R_3=OH$

New organo-transition metal electrocatalysts for reduction of carbon dioxide

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The depletion of fossil carbon sources together with the increasing global energy consumption demand alternative ways for the sustainable production of fuels and chemicals. The reduction of CO_2 to useful products can be achieved using molecular organometallic catalysts.[1] Electrochemical CO_2 reduction could potentially complete the anthropogenic carbon cycle by the production of chemical manufacturing from CO_2. The ultimate goal is development of catalytic systems that can selectively convert CO_2 into value-added commodity chemicals.

Results will be presented in two parts. The first part will describe studies of the structure and electrochemistry of new complexes of rhenium(I) and ruthenium(II) with benzimidazolium- (bi^+) substituted phenanthroline (phen) ligands, namely $[Re(CO)_3(phenbi^+)Cl][PF_6]$ and $[Ru(tpy^*)(phenbi^+)][PF_6]_2$, ($tpy^*$ = 4,4',4"-tri-*t*-butyl-2,2':6',2"-terpyridine). The complexes selectively catalyse the electroreduction of CO_2 to CO. The pronounced influence of the benzimidazolium substitution on TOF's and on the reduction potential for electrocatalysis will be highlighted.

In the second part, new metal pincer complexes inspired by the active site of the ubiquitous bacterial enzyme lactate racemase (LarA) will be described. Very recently, LarA was characterized as a Ni-dependent enzyme that contains a nickel pincer (SCS)Ni active site.[2, 3] It was proposed that the pincer ligand could reversibly capture a hydride from lactate at a pyridinium-derived carbon atom coordinated to the nickel ion. Several novel bis(thioamido)pyridinium ligands inspired by LarA have been prepared (*e.g.*, Figure 1) and a wide range of metal complexes made with a view to studying hydride transfer reactions, including with carbon dioxide.

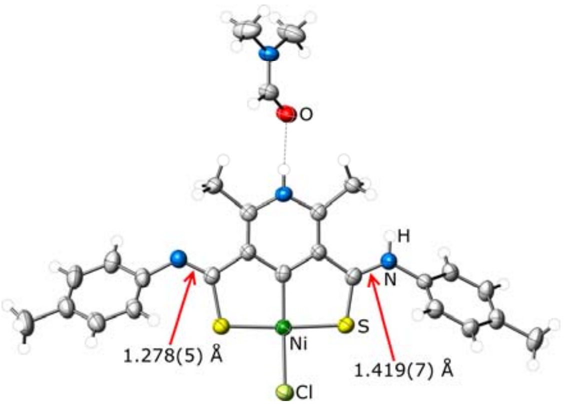

Figure 1. Solid-state structure of a newly synthesized (SCS)Ni complex with thermal ellipsoids set at 50% probability at 150 K.

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Nitromethane-Mediated, Three-Component Synthesis of β-Enaminones and Their Photochemical Properties

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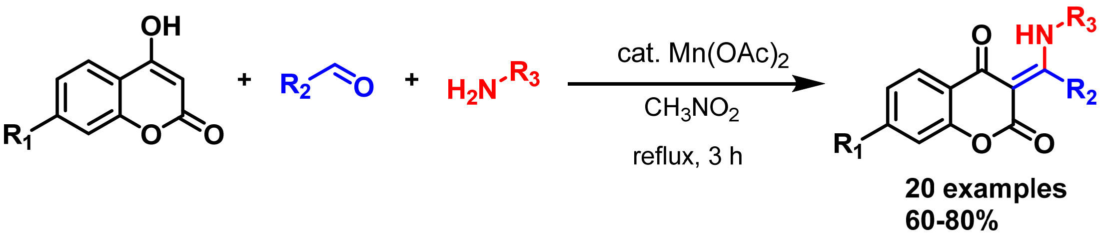
β-Enaminones are widely used as a building block or synthon for the preparation of many biologically active compounds.[1] Compounds featuring the β-enaminones or enamine-diketone possess many biological activities like antibacterial, anti-inflammatory, antiaggregant, antiischemic, antileukemia and other types of physiological activities. Herein we would like to report the $Mn(OAc)_2$-catalyzed coupling of 4-hydroxycoumarin with aromatic aldehyde and primary amine in nitromethane to obtain the library of β-enaminones in good to high yields. The synthesis, substrate scope, and mechanism of this three-component reaction along with the photochemical properties of the prepared compounds will be presented.[2]



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N-Methylation of Amines Using CO_2 and Rh(I) Catalysts

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N-Methylamines are an important class of biologically relevant compounds. They are present in many pharmaceuticals, dye molecules and agrochemicals. The traditional synthesis of methylamines relies heavily on the use of toxic reagents, e.g. methyl iodide or dimethyl sulphate,[1] which present significant hazards on an industrial scale. As such, a benign carbon source is sought after which allows the mass production of methylamines to be undertaken using a safer, more environmentally benign procedure. Carbon dioxide (CO_2) is a potential one carbon source that is non-hazardous, abundant and inexpensive. Due to the inertness of CO_2, harsh reaction conditions such as elevated temperatures and pressures are often required in order to react CO_2 with a substrate. This can be circumvented by the use of transition metal catalysts which promote the activation of either CO_2 or the substrate molecules in the reaction.[2]

Here, we present transition metal catalysed *N*-methylation of amines using CO_2 as the carbon source, and hydrosilanes as reductants. We found that Rh(I) complexes bearing PCP pincer ligands ($[RhCl\{\kappa^3\text{-}P,C,P'{=}C(NCH_2PCy_2)_2C_{10}H_8\}]$ (**1**) and $[RhCl\{\kappa^3\text{-}P,C,P'{=}C(NCH_2PPh_2)_2C_{10}H_8\}]$) (**2**),[3] which have the capability of activating Si-H bonds to reduce CO_2 are effective catalysts for the reaction. Methylamines bearing alkyl, aryl and other reducible functional groups have been obtained using Rh(I) complexes **1** and **2** as catalysts to promote the *N*-methylation reaction, at 1 atm of CO_2 and 25-90 °C. Product selectivity which favours the formation of monomethylated amines has been achieved by a prudent combination of solvents, reductants, and reaction temperatures.

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Noncovalent Binding of PAHs with Genetic Bases Reducing ARG Transfer

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Polycyclic aromatic hydrocarbons (PAHs) and antibiotic resistant plasmids (Arps) in the environment pose a serious threat to human health and ecological security. Combined PAH-Arp pollution has aroused much public concern. It is necessary to understand the fundamentals of PAH-Arp interactions prior to assessing their underlying environmental risks. In the present study, we assessed the effect of ampicillin resistance genes (Args) on representative PAHs phenanthrene/pyrene, revealing the noncovalent mechanism that inhibits the expression of Args in plasmid (pUC19). Results show that with plasmid exposed to the test PAHs, there is inefficient Arg expression in an E. coli host. In the absence of PAHs, the efficiency is 4.7 log units. However, the efficiency decreases to 3.72–3.14 log units with increasing phenanthrene/pyrene concentrations up to to 50 mg/L. Evidence from fluorescence titration, HPLC-MS, XPS, FTIR, and quantum computation suggests that tested PAHs physically intercalate into duplex regions of denatured DNA, combining with adenine constituents in plasmid. This physical combination damages the structure of plasmid, consequently restraining the expression of Args. Most importantly, information obtained from the study may provide a theoretical foundation for revealing the principle of combined PAH-Arp pollution, which has great significance for controlling this pollution and protecting ecological security.

Novel Agents Targeting Sphingolipid Signalling

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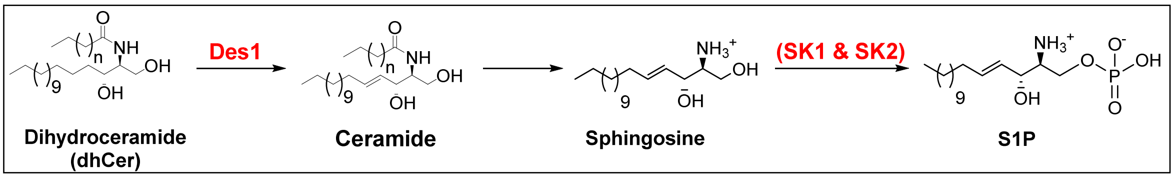
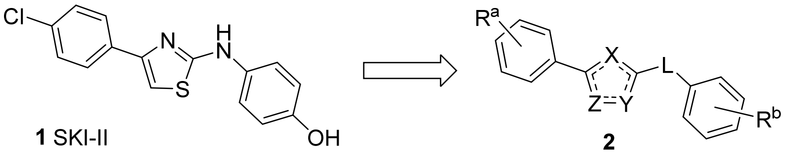
In recent years, the sphingolipid signalling pathway has been implicated in numerous disease states (e.g. cancer, fibrosis, inflammation and autoimmunity), through increased levels of lipid signalling molecule sphingosine-1-phosphate (S1P)[1]. As S1P expression is regulated by sphingosine kinases SK1 and SK2, SK1/2 inhibition has gained attention in the treatment of these conditions. In 2003 French *et al.* discovered the moderately active SK1/2 inhibitor **1** (SKI-II) in a high-throughput screen. **1** is a dual inhibitor of both SK1 and SK2, and promoter of SK1 proteasomal degradation. More recently (2014), in a study by Cingolani, F. *et al*, **1** has been involved in dihydroceramide desaturase (Des1) inhibition, an upstream enzyme in the sphingolipid metabolic pathway. We have undertaken a scaffold-hopping approach **(2)** in the optimisation of **1** to remove current metabolic liabilities and improve solubility, as well as increase activity in both cancer and fibrosis assays. In these studies it was observed that no correlation between SK1/2 inhibition and ant-proliferative and antifibrotic activity exists and the activity in these phenotypic assays is owed to Des1 inhibition.[2] Further optimisation of **1** as a Des1 inhibitor has been undertaken, giving potent and selective inhibitors for validating Des1 as a viable target for the treatment of prostate cancer and fibrosis.





1 SKI-II

IC_{50} SK1 = 30 μM
IC_{50} SK2 = 16 μM
IC_{50} Des1 = 0.8 μM

2

Potent and selective drug-like inhibitors of SK1, SK2 and Des1

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NOVEL RING FUSED FLAVONOID SYSTEMS DERIVED FROM *ORTHO*-QUINONE METHIDES

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Flavonoids are naturally occurring molecules that have been shown to exhibit a wide range of biological activities including anticancer, and anti-inflammatory properties. However, the flavonoids suffer from low bioavailability, which limits their overall potential as anticancer agents. One of the methods to overcome this limitation is through structural modification. In this study, the flavonoids, flavanone and isoflavene, were structural modified through the introduction of additional fused-ring systems *via* *ortho*-quinone methide intermediates (*o*-QM). These can readily undergo a [4+2] cycloaddition through an inverse electron-demand Diels–Alder reaction with electron-rich dienophiles. A regioselective Mannich reaction using bis-(*N,N*-dimethylamino)methane was employed to generate the C6-substituted *o*-QM isoflavene precursor. Similar Mannich reaction of 6-hydroxyflavanone and 7-hydroxyflavanone led to the C5 and C8-substituted analogues, respectively. The *o*-QM intermediates were subsequently generated *in situ* through thermal elimination of the dimethylamino functionality and were reacted with various dienophiles to produce novel flavonoids with fused-ring systems. Twelve novel flavanone and six novel isoflavene analogues were successfully synthesised. The X-ray crystal structure of the isoflavene analogue with the furan ring revealed the unique bend shape of the additional ring system. The anticancer properties of these novel fused-ring systems are currently being investigated.

One-Dimensional Nanomaterials for Energy Storage

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ABSTRACT TEXT

One-dimensional nanomaterials can offer large surface area, facile strain relaxation upon cycling and efficient electron transport pathway to achieve high electrochemical performance. Hence, nanowires have attracted increasing interest in energy related fields. We designed a single nanowire electrochemical device for in situ probing the direct relationship between electrical transport, structure, and electrochemical properties of the single nanowire electrode to understand intrinsic reason of capacity fading. The results show that during the electrochemical reaction, conductivity of the nanowire electrode decreased, which limits the cycle life of the devices. We have also fabricated hierarchical $MnMoO_4/CoMoO_4$ heterostructured nanowires by combining "oriented attachment" and "self-assembly". The asymmetric supercapacitors based on the hierarchical heterostructured nanowires show a high specific capacitance and good reversibility with a cycling efficiency of 98% after 1,000 cycles. Then, general synthesis of complex nanotubes was designed by gradient electrospinning, including $Li_3V_2(PO_4)_3$, $Na_{0.7}Fe_{0.7}Mn_{0.3}O_2$ and Co_3O_4 mesoporous nanotubes, which exhibit ultrastable electrochemical performance when used in lithium-ion batteries, sodium-ion batteries and supercapacitors, respectively. Recently, we have successfully fabricated a field-tuned hydrogen evolution reaction (HER) device with an individual MoS_2 nanosheet to explore the impact of field effect on catalysis. We have also constructed a new-type carbon coated $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ interconnected nanowires through a simply electrospinning method. The interconnected nanowires exhibit a discharge capacity of 101 mAh g^{-1} after 60 cycles, when measured as a cathode for K-ion batteries. Our work presented here can inspire new thought in constructing novel one-dimensional structures and accelerate the development of energy storage applications.

Optimisation of *Ec*DsbA Inhibitors by Fragment-Based Drug Design

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Abstract

Multi-drug resistant strains of bacteria are on the rise creating a need for the development of novel antimicrobials (W.H.O, 2014). Targeting bacterial virulence rather than viability has been proposed to slow the development of resistance and the diversity of virulence factors in different bacteria provides many novel anti-virulence targets (Rasko, 2010). DsbA is a key regulator of virulence which is required for the correct folding of many virulence factors and is found in many gram-negative bacteria (Heras, 2009), making it an attractive drug target. Due to its shallow and hydrophobic groove *Escherichia coli* DsbA (*Ec*DsbA) has previously been challenging to inhibit with small molecule compounds. Consequentially, Fragment-Based Drug Design (FBDD) was utilised to identify starting points in our efforts to generate inhibitors as it is popular for the optimisation of drugs for difficult to drug targets (Erlanson, 2016). The addition of reactive functional groups to fragments that bind to *Ec*DsbA has the potential to generate compounds with the ability to selectively covalently modify the active site of DsbA. In the current presentation I will describe our work to produce compounds that react covalently with *Ec*DsbA, assess their inhibitory activity and to evaluate their utility as chemical probes to study kinetics and enzymatic activity of *Ec*DsbA.

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Optimised Reactions for Thiol Probes to Detect Electrophilic Natural Products

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New methods are urgently needed to find novel natural products as structural leads for the development of new drugs against emerging diseases like cancer and multi-resistant bacterial infections. Here, we introduce a reactivity-guided drug discovery approach for electrophilic natural products, a therapeutically-relevant class of natural products that covalently modifies their cellular targets, in crude extracts. Using carefully designed halogenated aromatic reagents, the process furnishes derivatives that are UV-active and highly conspicuous via mass spectrometry by virtue of an isotopically-unique bromine or chlorine tag. In addition to the identification of high-value metabolites, the process facilitates the difficult task of structure elucidation by providing derivatives that are primed for X-ray crystallographic analysis. We show that a cysteine probe efficiently and chemoselectively labels enone-, -lactam-, and -lactone-based electrophilic natural products (parthenolide, andrographolide, wortmannin, penicillin G, salinosporamide), whilst a thiophenol probe preferentially labels epoxide-based electrophilic natural products (triptolide, epoxomicin, eponemycin, cyclomarin, salinamide). Using the optimized method we were able to detect and isolate the epoxide-bearing natural product tirandalydigin from Salinispora and thereby link an orphan gene cluster to its gene product.

Optimised reactions for thiol probes are also being developed to establish a HTS-like system.

Assessment of Orbital-Optimisation for Double-Hybrid Density Functionals

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Orbital-optimisation for Møller-Plesset Perturbation Theory (MP-PT) has been shown to be useful for the description of open-shell systems [1]. In addition, it is established that double-hybrid density functionals (DHDFs) are the most robust and accurate class of density functionals for molecular thermochemistry, even surpassing MP-PT approaches [2].

DHDFs contain a portion of correlation energy given by second-order Møller-Plesset Perturbation Theory (MP2), obtained from Kohn-Sham orbitals, thus orbital-optimisation can also be achieved for DHDFs. Indeed, preliminary studies suggest that orbital-optimisation could be a viable technique to improve DHDFs [3]. However, these studies were limited to three 'non-empirical' DHDFs that were all based on Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals. There have not been any extensive studies on orbital-optimisation for DHDFs that have other underlying exchange and correlation functionals and have higher accuracy than PBE-based DHDFs.

This presentation discusses orbital-optimisation for DHDFs, MP2 and its spin-component-scaled and spin-opposite-scaled variants (SCS-MP2 and SOS-MP2, respectively) for 19 benchmark sets comprising thermochemistry, kinetics and non-covalent interactions, as well as 3 other sets [4].

The overall effect of orbital-optimisation on calculations for closed-shell systems is found to be mostly negligible for the DHDFs and for SCS/SOS-MP2. In addition, orbital-optimisation overall worsens MP2 calculations. However, orbital-optimisation on calculations for open-shell systems improves SCS-MP2 and SOS-MP2, and slightly improves some DHDFs.

Our study therefore shows that orbital-optimisation may not be justified for DHDFs in general, despite earlier suggestions in the literature [3]. Instead, other routes may have to be followed to further improve the DHDF approach.

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ENTROPY, DISORDER AND DELOCALISATION ENABLE CHARGE SEPARATION IN ORGANIC SOLAR CELLS

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Organic solar cells promise cheap and lightweight renewable energy. However, charge generation in these devices is not well understood, making it difficult to systematically improve device performance. In particular, a vigorous debate surrounds how the positive and negative electric charges overcome their mutual attraction to form an electric current, sometimes with near-unity efficiency and on a sub-picosecond timescale. In typical models, the Coulomb binding between the electron and the hole can exceed the thermal energy $k_B T$ by an order of magnitude, which would make it impossible for the charges to separate before recombining. We consider the role of entropy both in the worst-case situation of localised carriers, and also with delocalised charges.

Firstly, we consider the entropic contribution to charge separation in the presence of energetic disorder for localised charges [1]. We find that for moderate amounts of disorder, the barrier is reduced to about $k_B T$ or eliminated altogether. Therefore, the charges are usually not thermodynamically bound at all and could separate spontaneously if the kinetics otherwise allowed it.

Accounting for delocalised charges over several molecules strengthens our result by further reducing the barrier to charge separation. Delocalisation lowers the mutual attraction of the charges at the interface by essentially allowing them to be further apart. When delocalisation is considered together with disorder and entropy, the thermodynamic barrier to charge separation is not prohibitively large as previously thought. Our work is discussed in context with recent experiments that are consistent with our explanation of charge separation.

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Organic synthesis of Spirooxindolo pyrrolizidines

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ABSTRACT

Two new spirooxindolo pyrrolidine compounds, analogues to the bioactive alkaloid structures found in the Uncaria Rhynchophylla plant, were synthesized from isatin (3) and proline (4) and an α, β-unsubstituted electrophile, following multicomponent methodology. The electrophiles successfully reacted were ethyl methacrylate and 3,4-methylenedioxyphenyl-2-nitropropene. An investigation into the scope of this reaction and its compatibility with functional groups has been carried out. The effect of solvent and temperature on the reaction was also examined. Products and a proposed intermediate were characterised using ^{1}H and ^{13}C NMR, FT-IR, MS and melting point.

Phonon Induced Sub-Bandgap Absorption in Cuprous Oxide Captures a Bit More Sunlight

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The emission of phonons from electron–hole plasma is the primary limit on the efficiency of photo-voltaic devices operating above the bandgap. In cuprous oxide (Cu_2O) there is no luminescence from electron–hole plasma. Therefore, we searched for optical phonons emitted by energetic charge carriers using phonon-to-exciton upconversion transitions. We found 14 meV phonons with a lifetime of 0.916 ± 0.008 ps and 79 meV phonons that are longer lived and overrepresented. It is surprising that the higher energy phonon has a longer lifetime.

The phonons we measured originate from relaxation of free carriers towards the conduction band minimum. This relaxation process is an important factor that caps the high theoretical solar energy conversion efficiency of cuprous oxide, a high elemental abundance, nontoxic semiconductor. Phonon emission can remove all charge carrier energy that is above the bandgap. We have captured phononic waste heat and light that is usually transmitted. We stored the energy in excitons. If these additional excitons can be utilised in future photovoltaic devices, it will increase the efficiency of solar energy conversion.

This presentation will be based on our paper:
Frazer, L., Schaller, R. D., Chang, K. B., Chernatynskiy, A., Poeppelmeier, K. R., Phys. Chem. Chem. Phys., 2017, **19**, 1151.

PHOTOCATHODIC PROTECTION EFFECT OF TiO_2 NANOTUBE FILMS ON STAINLESS STEEL

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TiO_2 semiconductor films as photoanodes can provide photocathodic protection for metals, which has inviting prospects. Therefore, preparations and applications of TiO_2 films have attracted considerable attention of corrosion researchers for corrosion control of metals. In this work, the TiO_2 nanotube films were prepared by anodization under different conditions, and their photoelectrochemical performances were studied.

TiO_2 nanotube films were prepared on the cleaned Ti foils by anodization at 20 V for 30 min in a two-electrode cell with different electrolyte solutions. After the anodization, the specimens were annealed at 450°C for 2 h. Characterization of the films was accomplished by scanning electron microscopy, X-ray diffraction, and UV-vis spectroscopy. Photoelectrochemical measurements were conducted by a home-assembled photoelectrochemical measurement system, which includes a photoelectrochemical cell with a 0.5 M NaOH solution and a corrosion cell with a 0.5 M NaCl solution. The photocathodic protection effects of the films were investigated by detecting the potential change of 403 stainless steel in the cell coupled to the film in the photoelectrochemical cell.

The results indicated that the electrolyte had an important effect on the morphologies and performances of the TiO_2 nanotube films. A well-ordered TiO_2 nanotube film was fabricated by the anodization in a glycerol solution with 40 vol% water and 0.5 wt% NH_4F. When illuminated, the film made the potential of the coupled 403 stainless steel decrease by 400 mV, showing a good photocathodic protection effect.

Acknowledgements

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Photohydroxylated ZnS Nanobelts with High Photocatalytic Activity

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Nowadays, the environmental concern from organic pollutant have been grown. Thus, environmental remediation and energy conversion using solar light have gained extensive interest. As a part of environmental remediation, the decomposition of organic water pollutants using photocatalytic nanomaterials has been studied recently. In particular, metal sulfides have attracted significant attention in photocatalysis due to their suitable band gap and catalytic function. ZnS have been received extensive attention as photocatalyst materials because of their unique properties such as the rapid generation of electron–hole pairs by photoexcitation and the high reduction potential of conduction band. However, because ZnS is direct band-gap semiconductor material, the recombination of excited electrons and holes is very fast. To hinder the recombination of charge carriers and to increase the charge-carrier lifetime, we have formed $Zn(OH)_2$ on the surface of the ZnS nanobelts via facile photochemical method. Hydroxyl radicals (·OH) formed by decomposition of hydrogen peroxide by UV light react with the surface of ZnS to form $Zn(OH)_2$. Heterojunction formed between ZnS and $Zn(OH)_2$ and surface hydroxyl functional groups separates charges effectively, and increases the lifetime of the excited charges. We have tested the photocatalytic efficiency of each sample via degradation test of 4-nitrophenol under Xenon-lamp irradiation. The optimized sample has showed 5.5 times higher photocatalytic activity compared to pristine ZnS nanobelts. Also, we have revealed the photocatalytic mechanism by monitoring reactive species using radical scavengers such as p-benzoquinone ($\cdot O_2^-$) and isopropyl alcohol (·OH).

Photoredox Catalysis: Enabling the Mild and Chemoselective Reduction of Ketimines.

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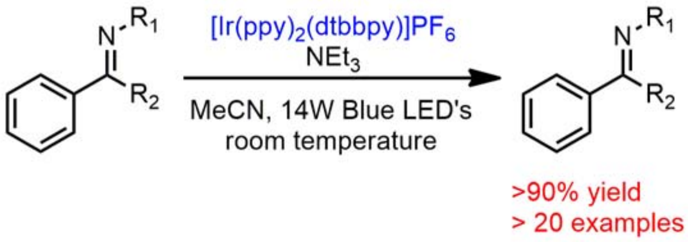
The reduction of imines represents a fundamental transformation that provides direct access to valuable 1° and 2° amines important to the development of pharmaceutical, agrochemical and fine chemical products. Traditional methods engaged for the reduction of imine mandate forcing conditions that limit functional group tolerance and chemoselectivity.

In this presentation, we report a new method enabling the photocatalytic reduction of ketimines via visible-light photoredox catalysis[1,2]. This transformation is achieved at mild conditions through the use of a poly-pyridine based iridium catalyst and triethylamine as a hydrogen source and is hypothesised to occur in a proton coupled electron transfer process.

This method furnishes secondary amines in high to excellent yields with broad functional group tolerance and short reaction times. Moreover, we demonstrate unprecedented chemoselectivity not available to traditional approaches.



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pH-responsive in-chain drug-polymer conjugate micelles for controlled delivery of gossypol

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Gossypol is a polyphenolic binaphthyl dialdehyde isolated from cotton seed. Gossypol has been reported as a potent antineoplastic agent that is cytotoxic towards a variety of mammalian cancer cell lines. Studies with colon carcinoma cell lines identified that gossypol inhibits colony formation and induces cellular apoptosis by binding with antiapoptotic proteins (Bcl-2 and Mcl-1). Gossypol is also of interest due to its glycolysis inhibition properties through inactivation of lactose dehydrogenase (LDH) in different cancer cell lines. Gossypol also possesses antiviral, antimalarial, and antifungal properties. However, the practical use of gossypol is restricted due to systemic toxicities including, hepatotoxicity and genotoxicity. The presence of the dialdehyde group that enables nonspecific binding with lysine residues in different enzymes is responsible for systemic toxicity of gossypol.

In this study, we introduce a novel approach to decrease the systemic toxicity of gossypol through incorporation into a pH sensitive delivery system. Initially, gossypol-imine copolymers with aldehyde end-groups were synthesized via step-growth polymerisation using gossypol and diamines as monomers. The gossypol-imine copolymers were then conjugated with poly(ethylene glycol) monoamine to afford an amphiphilic block copolymer capable of self-assembling into micelles in aqueous medium. Hydrolysis studies revealed that the micelles hydrolysed readily at pH 5.4 and were stable at pH 7.4. The pH sensitive nature of the in-chain gossypol polymers and their ability to form stable micelles opens the opportunity for controlled delivery of gossypol in cancer treatment as well as other diseases such as HIV or malaria.

pH-Switchable Nitroxide agents

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Nitroxides are persistent free radicals, which reversibly undergo redox reactions, and trap carbon centred radicals. The novel chemical properties of nitroxides results in a wide range of practical applications, including nitroxide mediated polymerisation. However, current alkoxyamines only thermally decompose to produce nitroxides under high temperature. At these temperatures there are many potential breakdown pathways[1], reducing the utility of nitroxide agents in both academia and industry. Previous computational and synthetic studies have suggested that the incorporation of a charged functionality allows for a reduction in reaction temperature[2,3]. Current work enhances this field of research through the incorporation of a radical initiator group onto a pH-switchable low temperature nitroxide agent. Consequently, allowing for the initiation and mediation of radical reactions using a single reagent. This presentation will outline our recent experimental results in this direction.

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pH-Switchable Organocatalysis

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ABSTRACT TEXT

Nearly 20 years ago, Shaik and co-workers theorised that it should be possible to accelerate non-redox reactions in the presence of an electric field, due to the ability of the field to stabilize charge-separated resonance contributors. [For a review see Shaik et al. Nat. Chem. 2016] However, there was one major drawback: for catalysis, the electric field must be suitably aligned relative to the reaction centre. As such, it was not until recently that this effect was realised experimentally, using scanning tunnelling microscopy and surface chemistry techniques to provide the oriented electric field. [Aragones et al. Nature 2016] Unfortunately, this is not a feasible technique for bulk-solution phase chemistry. To broaden the scope of electrostatic catalysis, we have proposed that the electric field be instead provided by charged functional groups on key reaction species [Gryn'ova et al. Nat. Chem. 2013]. An advantage of this approach is that, if the charge is produced by acid/base chemistry, the effect will be pH-switchable. Organocatalysts have been the subject of intense attention for almost 20 years, thanks largely to their ease of synthesis, low toxicity and cost. Here we present a systematic study of the effect of charged functional groups on their activity with a view towards pH-switchable catalyst design.

Phytochemical Investigations of *Eremophila Sturtii* and *Eremophila Mitchellii*

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ABSTRACT

Eremophila sturtii and *Eremophila mitchellii* are found in the arid and temperate regions of Australia and due to similar appearances are often confused. Previous phytochemical investigations have described a series of tetracyclic sesquiterpenes named the mitchellenes that were reported to derive from *E. mitchellii* but are demonstrated conclusively here to be from *E. sturtii*. Another previous study reported to be of *E. sturtii* actually isolated serrulatic acid from the leaves of *E. mitchellii,* and the voucher specimen has now been redetermined to confirm these findings. These observations were made in the course of a study of the solvent extracts and hydrodistilled oils from the two species. The known mitchellene B was isolated from *E. sturtii* as well as two new analogues mitchellenes F and G. The structure of mitchellene F was confirmed by the first x-ray structure of a natural product with the mitchellene skeleton.

Pictonium Cations for Enhanced Mitochondrial Uptake

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Triphenyl phosphonium (TPP) cationic moieties are traditionally used to deliver a wide range of molecular cargo to mitochondria organelle.[1] However, benefits associated with the modification of this simple and widely used moiety used as a mitochondrial transporter remains unexplored. Our studies illustrate how rational modification of the commonly used TTP results in a significant increase in the delivery properties.

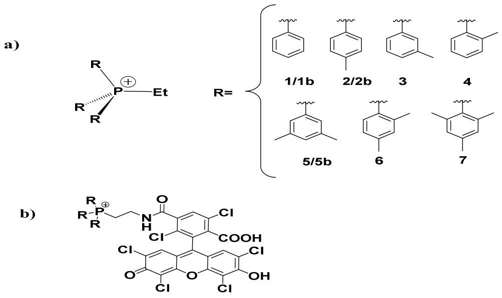

Figure 1: a) General structure of ethylphosphonium (**1**-**7**

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Piezo-like Electric Behavior of Electrospun Poly(lactic Acid) Nanoweb-Based Nanoenergy Harvester

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As electrospinning has been used as a powerful and useful method for the fabrication of piezoelectric polymeric materials such as PVDF and its copolymers, poly(L-lactic acid) (PLLA) nanofiber web was prepared through electrospinning for nanoenergy harvester and pressure sensor application. Considering the shear piezoelectricity of uniaxially drawn PLLA film or fiber, the piezoelectric signal cannot be generated from a conventional capacitor structure through exerting normal pressure, because $D_1=d_{14}T_4$ for PLLA film, i.e., piezoelectric charge (D_1) can be induced only by shear stress (T_4), not by normal stress (T_1). Nevertheless, we could obtain a very high piezo-like electric current from electrospun PLLA nanofiber web as in case of poled PVDF or P(VDF-TrFE) film or as-electrospun PVDF and P(VDF-TrFE) nanofiber webs by external pressure. This suggests that the electrospun PLLA nanofiber web can have preferentially oriented C=O dipoles, which induced piezoelectric charge as seen from poled PVDF or P(VDF-TrFE) film. However, poled PVDF or P(VDF-TrFE) loses piezoelectricity completely after annealing at 120 °C, since oriented CF_2 dipoles are randomized during annealing, whereas electrospun PLLA nanoweb showed piezo-like electricity even after annealing at 120 °C. Therefore, to identify the origin of piezoelectric charge induced by normal pressure exerted on electrospun PLLA nanofiber web, we proposed a new piezo-like electric mechanism in this study. More details are discussed in the presentation.

Acknowledgement: This work was supported by Industrial Strategic Technology Development Program Founded by Ministry of Trade, Industry and Energy (MOTIE), Korea (Grant No. 10044953 and 10047976).

POLYANILINE-MODIFIED CARBON ELECTRODE FOR ELECTROCHEMICAL DETERMINATION OF ASCORBIC ACID

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Abnormalities in the dosage of ascorbic acid (AA) may impose a great threat to human health. In this research, we devised an excellent electrochemical sensing unit based on polyaniline-modified carbon electrode (PANI-MCE). The sensing membrane was fabricated via *in-situ* polymerization process. The spectral and morphological properties of PANI-MCE were characterized using Fourier Transform Infrared (FTIR) spectrometer and Scanning Electron Microscope (SEM). The devised PANI-MCE presents good electrocatalytic properties, fast response time, and high reproducibility. Furthermore, the sensor exhibits a high sensitivity (18.713 uA mM^{-1}) and high repeatability (RSD= 8.52%), making it a good candidate for AA determination.

Preparation and characterization of vinylimidazole-based polymeric monolithic capillary LC column

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ABSTRACT TEXT

In order to analyze polar small molecule for environmental and food safety applications, several alkylmethacrylate-based (AlMA-based) monolithic columns have been developed in our laboratory. Although the developed AlMA-based columns could efficiently separate phenylurea herbicides as well as amphenicol and sulfonamide antibiotics, these reversed-phased stationary phases are not suitable for simultaneous analysis of analytes with different physical properties such as non-polar/weak-polar and polar/charged compounds. Therefore, the development of mixed-mode stationary phases with two or more retention mechanisms becomes inevitable to enhance separation capability for analytes with different physical properties. Ionic liquids (IL) have been incorporated into liquid chromatography stationary phases by immobilization on silica or monolith to perform separation with different retention mechanisms including hydrophobic, ion-exchange, hydrophilic, and π-π interactions. In this study, we applied 1-vinylimidazole (VIM) as the functional monomer to prepare a series of VIM-based IL-monolithic columns using various dimethacrylate/diacrylate as cross-linkers. The porosity, permeability, and column efficiency of synthesized IL-monolithic columns were characterized. A mixture of phenol derivatives was employed to evaluate the applicability of the VIM-based IL-monolithic columns for separating polar small molecules. Poly(VIM-*co*-1,10-decanediol dimethacrylate [poly(VIM-*co*-DDDMA)] IL-monolithic column exhibited good retention of phenol derivatives. The retention might be attributed to the enhanced hydrophobic interactions to the long alkyl bridge in DDDMA as well as the hydrogen-bonding and π-π interactions between the phenols and the imidazolium functionality on the stationary phase. Furthermore, six phenol derivatives were well resolved by the VIM-DDDMA IL-monolithic column with isocratic elution.

Preparation and photocatalytic hydrogen production of Organic-inorganic hybrid materials HO-TPA/TiO_2

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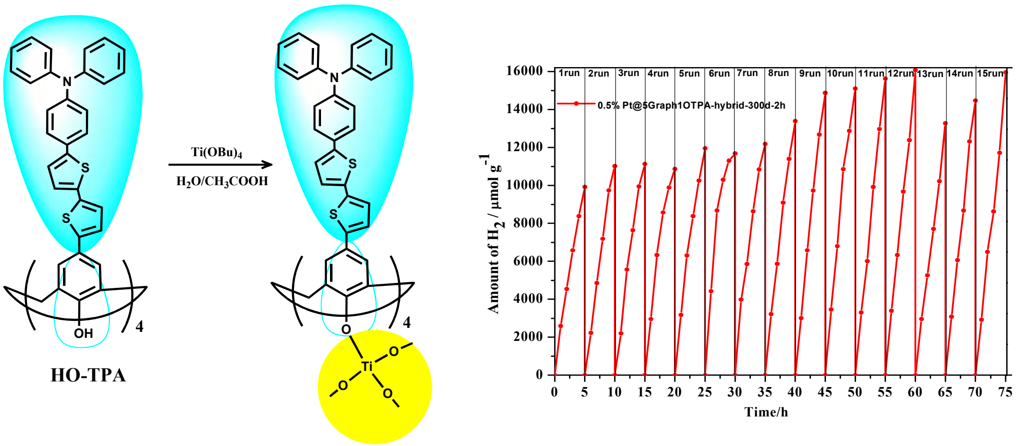
TiO_2 has been widely studied as a semiconductor photocatalyst for hydrogen production. [1] However, TiO_2 has narrow spectral response, fast photoelectron-hole recombination and low selective adsorption for the substrate, which limits its application in the visible-light catalysis. Calix[4]arene-based sensitizer with a cone structure has four light-harvesting units groups and anchoring groups in one molecule, which broaden the spectral response range, decrease molecule aggregation, suppress charge recombination, and improve the stability.[2] Combining the merits of both calix[4]arene and TiO_2, we have manufactured new organic-inorganic hybrid materials with calixarene-based dyes and titanium dioxide by a simple sol-gel method and studied their photocatalytic hydrogen production properties.[3]

In the paper, we have synthesized a calix[4]arene-based sensitizer **HO-TPA**, and then prepared a hybrid porous nanomaterial **HO-TPA**/TiO_2. The mass content of **HO-TPA** has been optimized and the growth mechanism of **HO-TPA**/TiO_2 has been explored. After loading the 0.5%wt Pt nanoparticles, Pt@**HO-TPA**/TiO_2 exhibited high H_2 production rate and good stability. The results show that the H_2 production rate under visible light irradiation ($\lambda \geq 420$ nm) was 3 mmol g^{-1} h^{-1} with triethanolamine as sacrifical agent and remained unchanged after 15 circle experiments.



(a) (b)

Fig.1 (a) synthesis of **HOTPA**/TiO_2 and (b) photocatalytic H_2 production over the recyclability of Pt@**HOTPA**/TiO_2 with 0.5 wt% Pt loading under visible light irradiation.

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Preparation and Splitting of Pure Toroidal States via Molecular Spintronics

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Controlling single-molecule degrees of freedom is crucial for the ultimate miniaturisation of electronics and spintronics components, and more ambitiously, the development of quantum computers. To this end, we theoretically investigated the ground state non-collinear spin-texture and spin-transport properties of triangular rings with on-site spins . In the limit of strong antiferromagnetic exchange and weak spin-orbit coupling, we found that non-collinear spin states with zero magnetic moment and non-zero toroidal moment, , can be prepared in these systems: (i) by spin-frustration only, even without any spin-orbit coupling; (ii) in the ground Kramers doublet resulting from weak spin-orbit splitting via Dzyaloshinskii-Moriya antiferromagnetic exchange coupling. Such states had previously only been found in molecules with strong spin-orbit coupling. We investigated the relationship between toroidal states and chiral spin states, characterised by the eigenvalues of the spin-chirality operator, . We found , meaning spin states cannot be both toroidal and chiral simultaneously. Finally, we developed a quantum transport model in the Coulomb-Blockade regime, for a three-terminal molecular spintronics device. A spin-current injected through a spin-polarised source electrode into the triangle is partially reversed upon scattering with the molecular toroidal states. This is a molecular spin-transfer torque effect, which may possibly be harnessed with a bias voltage to split the non-equilibrium populations of the and toroidal spin states. With this splitting, one could initialise a toroidal spin qubit for quantum computation. However, for such a device to operate successfully, it must be constructed according to our specifications for geometric and energetic parameters.

Preparation of Cyclopropyl Carbinols *via* Reductive Ring Opening of Ethyl-chloro-oxazinones

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The applications of cyclopropyl carbinols span a broad range of chemistry, with roots in both natural product chemistry and chemical synthesis. Natural products incorporating this moiety include the illudanes, aspterpenacids A and B, and cycloartane triterpenoids. Total syntheses utilising these substrates as intermediates include the synthesis of taxol and members of the epithilone family. Within synthetic organic methodology, cyclopropyl carbinols have been used to prepare conjugated dienes and ene-ynes, polycyclic-cyclobutanes, benzoxazines, benzo-azepines, vinyl-indolines, and aryl-fused-cyclohexadienes. While the wealth of chemical diversity attainable through the reaction of cyclopropyl carbinols is appealing, the versatility of these methodologies is hindered by limited access to functionalised cyclopropyl carbinols.

While investigating the reduction of previous 1,3-oxazin-4-enones prepared in our group, it was discovered that the treatment of these species with lithium aluminium hydride led to the ring-opening of the 1,3-oxazin-4-enone core, as well as the formation of a cyclopropyl moiety. The reaction scope and mechanistic details will be discussed, as will the application of these cyclopropyl carbinols in the context of prior synthetic methodologies.

Properties of double layered silicone for a wearable kinesiology tape

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ABSTRACT

Kinesiology tape can benefit a wide variety of musculoskeletal and sports injuries. Most of kinesiology tape is placed on skin with elastic adhesive. In this study, it is aimed to develop a clothes type kinesiology tape. For a wearable elastic therapeutic tape in cloth, a double layered silicone was developed. It is necessary for good adhesion to skin, strong property to bond fabric, and skin allergies relief. Bottom layer of the silicone is composed of liquid silicone rubber to bond fabric strongly. Top layer of the silicone consists of the mixture of a medical grade liquid silicone rubber and a pressure sensitive adhesive(PSA) for medical applications for microscopically lifting the skin. PSA was applied to compensate low viscosity and mechanical properties of top layered liquid silicone rubber. Adhesive performance to skin and bonding strength to fabric were tested. As a result, adhesive property to skin was 0.54 N/cm^2 and the bonding strength to fabric was 4.2 N/cm. These results indicate that the multifunctional silicone can bond a wearable fabric and lift skin as a kinesiology taping application.

Purple bacteria use quantum coherence to harvest light more efficiently

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Photosynthetic organisms harvest light using large arrays of organic molecules, whose couplings are often large enough that energy transfer through the arrays is partially coherent. However, making precise claims about the role of coherence in photosynthesis has been difficult because it requires expensive computational techniques.

We accelerated simulations of energy transport in photosynthetic complexes by orders of magnitude by exploiting the incoherent nature of the incident light, showing that quantum coherence can enhance light harvesting even in incoherent sunlight [1, 2]. The faster simulations allow us to screen many alternative scenarios—by changing couplings, energy offsets, geometries, etc.—to determine whether coherence is indeed important for biological function or is merely an evolutionary accident [3, 4].

Here, we report the most statistically significant quantum enhancement identified in a photosynthetic complex so far [4]. We show that the light-harvesting apparatus of purple bacteria is five standard deviations more efficient than would be expected by chance alone, and that the enhancement is largely due to supertransfer, a cooperative enhancement of energy transfer due to coherent delocalisation [4].

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Quantum Dot Hetero-Assemblies Increasing Triplet Exciton Energy Harvesting Efficiency

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One of the reasons for the limited efficiency of photovoltaic devices is that the portion of sunlight with energy that is high above the bandgap of the solar cell is partially lost because of thermalisation. This study is attempting to use exciton transfer of Singlet Fission (SF) generated triplets through Quantum Dot (QD) hetero-assemblies to more efficiently harvest normally underutilised higher energy light. This research presents the opportunity to increase the quantum yield of photovoltaic devices as well as gain a more in-depth understanding of exciton transfer.

SF involves splitting a single photon of light into two triplet excitons which are more useful than a singlet exciton which loses its excess energy as heat. The linked hetero-assemblies consist of smaller donor and larger acceptor PbS Dots, with the unidirectional exciton transfer occurring due to an energy difference between the dots.

Using anthracene as the source of SF, we will attempt to use Forster Resonance Energy Transfer (FRET) to shift triplets first the donor QD's then to the acceptors. The reasoning behind the dual transfer is that the donor QD’s are unpassivated and while extremely effective at exciton transfer they are poor photo-emitters. We hypothesize that by using the donor QD’s as an intermediate rather than an emitter, any loss of efficiency during the transfer between the donor and acceptor QD’s will be overshadowed by the increased photoluminescence yield of the acceptor QD’s.

RADIOANALYTICAL CHEMISTRY CAPABILITY AT ANSTO

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ANSTO's Nuclear Stewardship, Radioanalytical Chemistry Capability (RACC) group combines radioanalytical chemistry and medium level gamma-ray spectrometry. This group has expertise in the measurement of natural and anthropogenic radionuclides in samples from pristine to contaminated environments.

Actinide analysis uses an optimised method to separate and quantify a series of radionuclides. This involves complex radiochemical techniques and various combinations of ion exchange chromatography resins (Eichrom®). Routinely, these are employed to separate actinides such as Am, Pu, Th, U as well as Sr isotopes. Actinides are measured using alpha spectrometry and Sr isotopes by liquid scintillation analysis (LSA) in Cherenkov counting mode. Tritium in fresh waters and leachate can be quantified using a rapid, small sample volume, three stage Eichrom® column followed by traditional LSA. Our LSA also operates in Cherenkov mode for quantification of $^{89/90}$Sr and ^{32}P. Natural (U series, Th series, K) and anthropogenic (^{241}Am, ^{137}Cs, ^{60}Co etc.) radionuclides in soil, sediment, vegetation, water and biota are quantified by gamma-ray spectrometry where n-type High Purity Germanium (HPGe) detectors with relative efficiencies of 15-50% are used.

RACC aims to develop and maintain specialist radioanalytical and experimental facilities utilising nuclear techniques to support ANSTO site essential services as well as investigations related to legacy nuclear sites in our region (Little Forest Legacy Site, Maralinga and Montebello Islands), radionuclides in the environment at or above typical environmental levels and the nuclear fuel cycle. RACC contributes to international and regional groups which underpin Australia's response to releases of radioactivity into the environment.

Rapid Access to N-(indol-2-yl)amides and N-(indol-3-yl)amides

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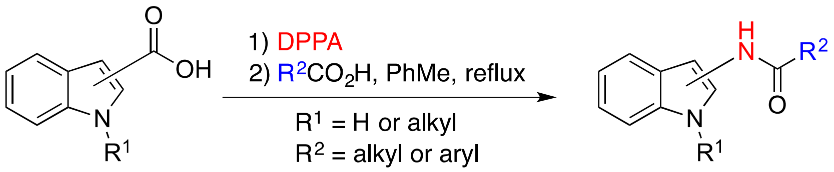
Preparation of *N*-(indol-2-yl)amides and *N*-(indol-3-yl)amides are scarce in the scientific literature due to unstable intermediates impeding current reported syntheses. We have employed cheap and readily available substrates in the Curtius rearrangement of indole-3-carboxazide to afford N-(indol-3-yl)amides. The reaction is observed for alkyl and aryl carboxylic acids and both *N*-substituted or free base indole derivatives are tolerated. This approach was extended to the preparation of N-(indol-2-yl)amides from the corresponding indole-2-carboxazides.



***N*-(indol-3-yl)amides (1)**
24 examples
up to 90% yield
***N*-(indol-2-yl)amides (2)**
15 examples
up to 91% yield

Reaction of Toxic Gases on Ag(111)-Supported Silicene

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ABSTRACT

Silicene is a new two-dimensional nanomaterial with many unique and interesting properties [1]. Due to its extreme thinness (on the nanoscale) and large lateral dimensions, it has potential applications as a gas sensor/storage material, or as a component in electronic devices.

Currently, the primary method to synthesize single layer silicene is to grow it on a substrate, such as Ag(111). The Si/Ag(111) system is highly reactive with oxygen, leading to oxidation of the silicene layer [2,3]. Little information, however, is known about the reaction of other gases with this system. While SO_2 and NH_3 have been shown to adsorb on the surface [4], only 1 orientation of these gases was presented. Further studies need to be performed in order to determine how different gases react with the surface, how strongly they bind and affect the charge distribution, and whether they dissociate on the surface.

In this work, density functional theory calculations and *ab initio* molecular dynamics simulations were used to examine the reaction of SO_2, NO_2 and H_2S on the Si/Ag(111) surface. It was shown that each gas can adsorb on the surface in different orientations and adsorption sites. NO_2 and SO_2 chemisorb on the surface, whereas H_2S physisorbs. SO_2 and H_2S adsorb associatively whereas NO_2 readily dissociates, producing adsorbed O and a gaseous NO molecule. At elevated temperatures the SO_2 and NO_2 remain bound to the surface poisoning it, while H_2S readily desorbs.

This work shows that Si/Ag(111) may provide useful properties for gas sensor or storage applications.

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Regenerative Photoactive Polymer Networks by Metal-Terpyridine Interaction: Toward Sustainable Photocatalysis

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ABSTRACT:

The design and synthesis of photoactive polymeric systems are important in regard to solar energy harvesting and utilization. Although many organic photoactive systems have been developed, they suffer from their inferior long-term stability. However, Nature utilizes self-regeneration system in order to sustain photosynthesis efficiency. Here, we synthesized photoactive polymeric thin films via iterative self-assembly using reversible metal-terpyridine (M-tpy) interactions. We envisioned that the reversible M-tpy interaction can be exploited to mimic Nature's self-repair system. In order to introduce tpy groups readily, we utilized cis-5-norbornene-exo-2,3-dicarboxylic anhydride, a norbornene derivatve, to which amine-functionalized tpy was coupled very easily. Ring-opening metathesis polymerization (ROMP) with tpy-norbornene monomers by Ru catalysts enabled the production of tpy-functionalized linear polymers and network ones. We will discuss here the several applications of tpy-functionalized polymers to photoactive thin films and regenerative photocatalytic systems.

REMARKABLE VISIBLE AND NEAR-INFRARED EMISSION OF LANTHANOID β-TRIKETONATE ASSEMBLIES

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Abstract

Lanthanoid complexes have been widely studied for their characteristic sharp and long-lived line-like emission. There has been notable interest in the design of luminescent lanthanoid metal complexes for applications in bioimaging, solar cells, and visible organic light emitting devices (OLEDs).[1] In comparison, near-infrared emitting OLEDs (NIR-OLEDs) have received less attention. We have been studying luminescent lanthanoid β-triketonate complexes and their applicability in OLEDs and NIR-OLEDs. Although there are many reports of lanthanoid complexes with β-diketonate ligands, the coordination of β-triketonate ligands to lanthanoids is relatively unexplored.[2-3] Different β-triketonate ligands, various co-ligands and alkali metals, have been used in order to study differences in the structure of the resulting lanthanoid complexes, and the effect on their visible and NIR photophysical properties. The results indicate that β-triketonate ligands are able to form assemblies of the lanthanoids with improved NIR emission, which rival previously reported species where ligands were perfluorinated or deuterated to minimise quenching.

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Renewable polymers from vegetable oils and sulfur capture heavy metals

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Inverse vulcanization was used to crosslink various vegetable oils (canola, sunflower olive and limonene) and their fatty acids with elemental sulfur producing renewable polymers for applications in heavy metal capture. As a mass-produced by-product of the petroleum industry, elemental sulfur is a readily available and inexpensive building block for co-polymerisation with renewable vegetable oils and their fatty acids. These reactions convert elemental sulfur, a yellow powder, into rubbery products with improved mechanical properties for capturing heavy metals which are a continuing environmental threat.

Representing Fragment 3D-Pharmacophore Space for Exhaustive Screening

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The key idea of fragment screening is that already a small selection of appropriate fragments (~10^3 cpds.) covers a much larger proportion of the overall chemical fragment space (~10^7 cpds.) than a typical high-throughput screening collection (10^5 – 10^6 cpds.) with respect to the drug-sized chemical space (~10^{63} cpds., *MW* < 500 Da). Moreover, in contrast to larger molecules, fragments may bypass strict steric requirements for the binding, leading to high hit rates up to 20%. For the same reason fragments often find a well-suited anchor positions leading to low-affinity yet highly efficient binding and making them excellent starting points for subsequent ligand design, with the inherent potential to reconstruct the larger lead- or drug-sized chemical space.

An optimal generic fragment library for diverse targets aims at fully exploiting the above described potential. Physicochemical requirements delineated by the rule of three (Ro3) are important for fragment binding. Beyond that, however, a fragment library will only meet the expectations if containing adequate molecules that bear diverse pharmacophores, are chemically evolvable and representative in order to yield high hit rates and facilitate fragment-to-lead evolution for generic targets, allowing to reconstruct the desired chemical space.

To complement our established in-house fragment library, which led to 70 (20%) crystallographic hits for endothiapepsin, we compiled a set of 1271 high-quality fragments with 3D-diverse pharmacophores suited for crystal soaking, immediate fragment-to-lead evolution, prepared for computer-aided subset selection and fragment-to-lead evolution.

REVERSIBLE NICKEL-IRON HYDROXYLPHOSPHATE CATALYSTS FOR HIGHTLY EFFICENT INTERMITTENT WATER SPLITTING

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ABSTRACT

Global scale application of water splitting technology for hydrogen fuel production and storage of intermittent renewable energy sources has called for the development of oxygen and hydrogen evolution catalysts that are inexpensive, efficient, robust, and can withstand frequent power interruptions and shutdowns. Here we show controlled electrodeposition of porous nickel-iron hydroxylphosphate (NiFe-PO_4) nanobelts onto the surface of macroporous nickel foams (NF) as a bifunctional composite catalyst for efficient whole cell water electrolysis. The NiFe-PO_4/NF electrode exhibits high catalytic activity towards water oxidation and water reduction in alkaline solutions, and is capable of delivering current densities of 20 and 800 mA cm^{-2} at overpotentials of 249 and 326 mV for oxygen evolution reaction (OER), current densities of 20 and 300 mA cm^{-2} at overpotentials of 135 and 208 mV for hydrogen evolution reaction (HER). Further, in a two-electrode water electrolytic cell, the bifunctional NiFe-PO_4/NF electrodes can achieve current densities of 20 and 100 mA cm^{-2} at cell voltages of only 1.68 and 1.91 V, respectively. Remarkably, the NiFe-PO_4/NF catalyst also exhibits prolonged stability under both continuous and intermittent electrolysis, and can be used for oxygen evolution and hydrogen evolution reversibly without degradation.The excellent catalytic activity, stability as well as the facile and scale-up fabrication process of the NiFe hydroxyphosphate catalyst makes it promising for use as a noble-metal-free water-splitting electrode for industrial water electrolysis.

Rhodium(I)-Catalyzed Asymmetric Carbene Insertion

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ABSTRACT

Transition metal-catalyzed C-H or X-H (X = O, N, S, Si) insertion of metal carbene stands for an excellent approach for the construction of C-C or C-X bonds. Among them, catalytic asymmetric carbene insertion into C-H bonds has been well defined, while the asymmetric C-X bond formation via metal carbene intermediate were developed only recently. The Rh(II), Cu(I)/(II), Ir(III), and Fe(II) with suitable chiral ligands are the most regularly used catalysts for these transformations. On the other hand, rhodium(I) complexes with diverse chiral ligands are efficient catalysts for various asymmetric reactions, however, the related Rh(I)−carbene chemistry is far less studied. Recently, our group succeeded in performing the asymmetric metal−carbene insertion into X−H (X = B, Si) bonds using Rh(I)/diene complexes as catalysts (Figure). In this presentation, these achievements as well as recent progress will be described.

Ruthenium-Hydride Benzimidazolidene Organohydride Conjugates in Chemical Reduction of CO2

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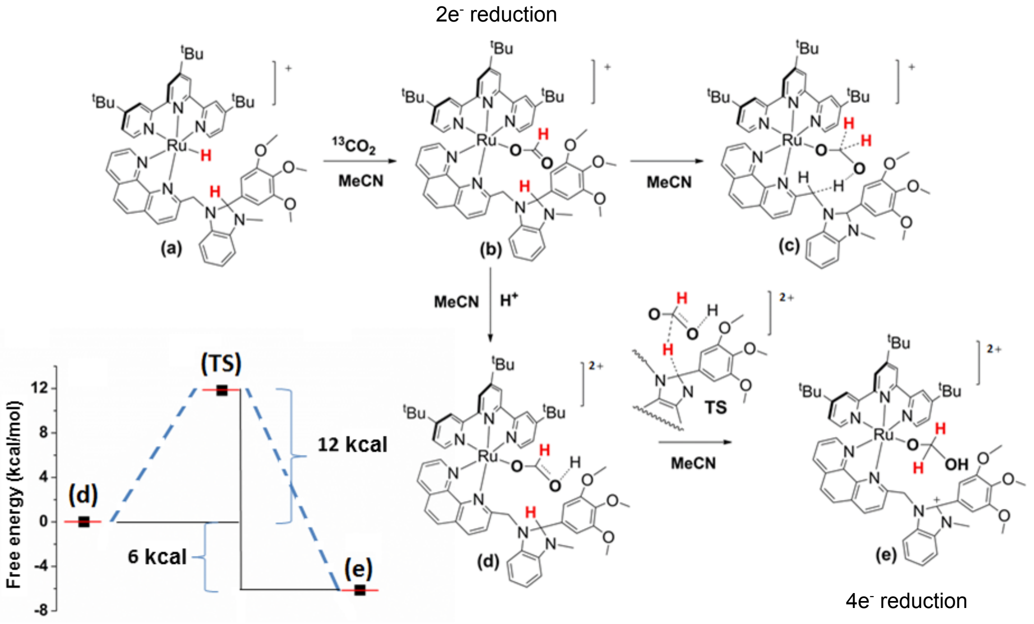
The adverse effects of ever increasing CO_2 level in the atmosphere have provided the impetus for an active field of modern day research: *The conversion of atmospheric CO_2 to value added materials*. Besides decreasing the CO_2 level in atmosphere, this research has the potential to provide useful resources such as fuel (for example water gas, methane, and methanol) and other valuable carbon containing materials (such as formic acid, formaldehyde) which can be further used in organic synthesis as well as for medicinal purposes.[1] Almost all direct processes for reduction of carbon dioxide that employ molecular catalysts stop at the two-electron ($2e^-$) level; that is formate/formic acid or carbon monoxide are the primary products.[2,3] It becomes very challenging to push the reduction beyond $2e^-$ reduction using molecular catalysts as it requires additional energy. Organohydrides may catalyse electroreduction of CO_2 beyond the $2e^-$ level.[c] Moreover a close proximity of metal hydride and an organohydride donor provide prospects for driving the reduction to the $4e^-$ level. In this regard ruthenium-hydride benzimidazolidene organohydride conjugates were synthesized and characterized. Chemical reduction of CO_2 was investigated using ^{13}C labelled CO_2. The products were characterized by NMR, UV-Vis and ESI-MS techniques. DFT investigations were carried out to understand the reaction barrier and possible ways to bring it forward.



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Screening Effects on van der Waals Interactions

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Van der Waals interactions are ubiquitous in the world, and have been recognized as critical to most important properties of natural matters including proteins and DNA (deoxyribonucleic acid). In chemical and biochemical environments, modern empirical approaches like Grimme's D3 method allow for fast evaluation of these forces in electronic-structure calculations. However, this and related methods are based on London's approximation to the van der Waals force as arising from pairwise-additive atomic fluctuations and polarizations. Recently, the Dobson classification was introduced to understand the shortcomings of such approaches, shortcomings particularly relevant for low-dimensional molecules and conductors such as graphene, C_{60}, large aromatic molecules, and nanotubes. An important experimental characterisation of non-additive effects was the recent demonstration the placing a graphene layer between a silica substrate and silica AFM tip switches off the van der Waals interaction between tip and substrate through a Faraday-cage screening effect. We develop computational models to understand this effect, comparing the pairwise-additive D3 method to the popular many-bond dispersion (MBD) method for treating screening, and a new method developed by Gould to include and improve not only these contributions but also those from long-range fluctuations (related to the Casimir effect).

Separation and Determination of Clenbuterol and Ractopamine Using Field-amplified on-line Sample Stacking Method by Capillary Zone Electrophoresis

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A rapid, simple and reliable capillary zone electrophoresis method was developed for the separation and determination of clenbuterol and ractopamine. A buffer solution of KH_2PO_4-Na_2HPO_4 (50 mM) with pH 7.20 was used as running buffer and the field-amplified sample stacking (FASS) technique was also applied to the on-line concentration of clenbuterol and ractopamine. Under the optimum conditions, clenbuterol and ractopamine were separated completely and determined with the correlation coefficient of 0.9994~0.9996. Both of the detection ranges (S/N=3) were located from 0.1 to 50 μg mL^{-1}. And the limit of detection was down to 20.0 ng mL^{-1} and 23.6 ng mL^{-1} for clenbuterol and ractopamine. The relative standard deviations (RSD) were less than 2.63% (run to run) and 3.73% (day to day) for peak area. Using the stacking measure, clenbuterol and ractopamine in spiked swine feed were successfully determined with the recovery of more than 95.4%.

Design and Synthesis of Short Amphiphilic Cationic Peptidomimetics Based on Biphenyl Backbone as Antibacterial Agents

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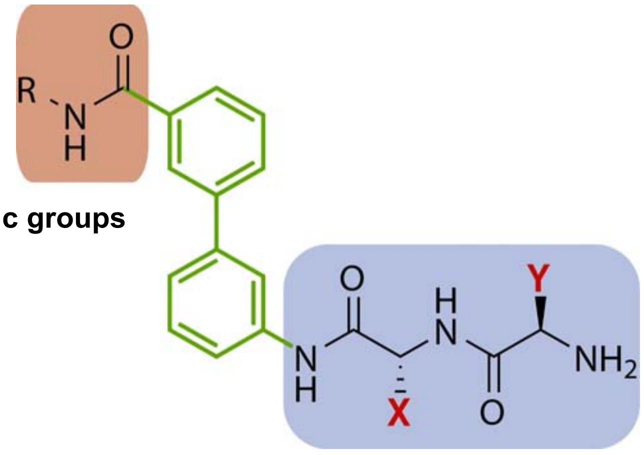
The discovery and development of antibiotics is a success story in medicine wherein countless lives have been saved in the past century. However, there is an urgent need for new classes of antibiotics to keep pace with rapid, inevitable onset of antibiotic resistance. Antimicrobial peptides (AMPs) are typically 10-50 amino acids in length and form part of the innate immune system in all classes of life forms including plants, insects, amphibians, fishes, birds, and mammals. Unlike conventional antibiotics, AMPs act via non-receptor interactions which make it difficult for the bacteria to develop resistance. Most cationic antimicrobial peptides possess rigid secondary structure and adopt an amphipathic conformation in such a way that their hydrophobic and hydrophilic amino acids aggregate on opposite faces of the molecular skeleton. Short peptidomimetics based on AMPs comprise one of the most effective approaches to new antibiotic discovery. In this work, we used representative hydrophobic, hydrophilic groups and a biphenyl backbone to design a library of amphipathic structures and investigated their antibacterial activity and mechanism of action. These peptidomimetics displayed good potency against *S.auerus* and were non-toxic towards human cells. The results of this study will be presented.



R = Hydrophilic groups

X, Y = Hydrophobic groups

Silicone Coated-Uniaxially Drawn PLA Film with Improved Piezoelectric Sensor Performance

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Polylactic acid (PLA) is well known as a biodegradable and biocompatible polymer with shear piezoelectric properties. The unique piezoelectricity of PLA is understood to originate from genuine chiral molecular conformation and helical structure aided by the transformation of 10_3 helical to 3_1 helical structure upon drawing film. In this study, we prepared uniaxially drawn PLA films with different draw ratios and investigated their piezoelectricity depending on draw ratio. We also measured birefringence of drawn PLA films and correlated the relationship between birefringence and piezoelectricity of ones. The film was cut in the direction of 45^o angle from the draw direction and was fabricated into a rectangular sensor followed by adhering conductive fabrics to top and bottom surfaces. The observed piezoelectric voltage of PLA sensor depends on draw ratio under tensile stress. The result indicates that more drawn PLA film sensor shows higher piezoelectric voltage signal. Moreover, to improve the piezoelectric sensor performance, the PLA film sensor was coated on both sides with silicone rubber. The silicone coated-PLA film sensors are sandwiched between the two elastic textile bands along the longitudinal direction, which is designated as physiological sensing belt (PSB). The silicone coated-PLA film sensor showed higher piezoelectric signal compared with PLA film sensor itself. PLA film-based PSBs can be applied to the mattress to measure the electrical signals generated by the elongation of the sensor during heartbeat and respiration. More details will be discussed in the presentation.

This work was supported by MOTIE, Korea (Grant No. 10047976 & 10044953).

Simple Preparation of Tetraepoxy Compound from Anthracene revealed in Spectroscopic Study

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Tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) has been widely used as single-electron transfer catalysts in photo-induced oxidation and reduction reactions. To explore and monitor various photoredox reactions, we designed and fabricated a reaction box equipped with a light-emitting diode (LED) as a photon source, and optical fibre connected to a charge-coupled device (CCD) spectrometer that enabled quantitative measurement of a portion of the emitted light from the reaction under progress. This provides us with insight into the activity of the photocatalyst and therefore the mechanism of the synthetic reactions. During our preliminary studies utilising this approach to explore the aerial oxidation of anthracene, we found an exceedingly simple approach to synthesise and isolate an interesting eight-electron oxidation product. The newly synthesised tetraepoxy compound has been characterised unambiguously from ^1H NMR, ^{13}C NMR, and single-crystal X-ray diffraction studies and a plausible mechanism for the reaction has been established.

Simultaneous determination of 12 sweeteners in foods by LC-MS/MS

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ABSTRACT

A simple, rapid and sensitive method for the simultaneous determination of 12 sweeteners [acesulfame potassium (ACS-K), advantame (ADV), alitame (AL), aspartame (ASP), cyclamate (CYC), dulcin (DUL), glycyrrhizic acid (GA), neotame (NEO), neohespheridin dihydrochalcone (NHDC), sodium saccharin (SAC), sucralose (SCL), stevioside (STV)] in foods by liquid chromatography/tandem mass spectrometry (LC-MS/MS) was developed. The chromatographic separation was performed on a Xbridge BEH (2.5 μm, 3 x 50 mm) column with gradient elution of 10 mM ammonium acetate in water and methanol. Sample preparation procedure consisting of sample dilution, addition of Carrez reagents and filtration is required before analysis. The analytical method was validated based on the following criteria: linearity, accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ). The validation results were satisfactory. The proposed method was successfully applied to the analysis of the sweeteners in some food products commonly consumed in South Korea.

Single-molecule magnets under Irradiation Work as Spin Pumps and Switches

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We theoretically investigate a single-molecule magnet (SMM) grafted to a quantum dot in contact with metallic electrodes. The SMM-dot region is immersed in a weak longitudinal static magnetic field opposed to the giant spin of the SMM and perturbed by the magnetic component of radiation propagating along its easy axis. We explore the steady state current voltage characteristics of the device when the source electrode is both non-polarised and fully spin-polarised. Without spin polarisation, we find that the SMM-dot hybrid acts as a spin pump, sequestering spin “up” current on the device and outputing spin “down” current to the electrodes; the effect is quenched at higher voltages. When the source electrode is spin-polarised we find that, even at zero bias voltage, a net current persists through the device with the spin current injected in the ferromagnetic source being reversed and amplified in the drain lead. The spin switching and spin pump effects occur at resonance between the frequency of the radiation and the energy required to tilt the giant spin of the SMM.

Size control of anodic alumina membrane for aerosol therapy

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ABSTRACT

Inhalation therapy has played a pivotal role in the vistas of pulmonary drug delivery since ancient times, as a way of relieving respiratory diseases. Particularly, pulmonary delivery of drugs has develop into an attractive target in the health care industry as the lung is capable of absorbing pharmaceuticals either for local deposition or for systemic delivery. These drug delivery techniques has made developed rapidly in the 1950s with the development of nebulizers and pressurized metered-dose inhalers. Nebulizers transform liquid formulations and suspension into medical aerosol. In the past few years, there have been advances in the development of new nebulizers that hold the promise to improve aerosol drug delivery to patients with pulmonary diseases. In this study, a simple method is presented for the morphology and the dimension controls of the free-standing nanoporous and microporous membrane without the utilization of any elaborated instrumental works. This simple control of the nanoporous membrane is accomplished only by applying the same typical two-step anodization process of the utilized aluminum templates from the previous simple plate-type aluminum substrate. Also, the microporous membrane was synthesized by lithography process and electroforming process. Morphology and structural properties of the various porous membranes are investigated by field emission scanning electron microscopy, high resolution transmission electron microscopy, x-ray diffraction.

SnO_2/ZnS Nanocomposites with High Photocatalytic Performances

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Heterojunction nanocomposites, where one semiconductor is partially coated by the other semiconductor, have received extraordinary attention as photocatalysis systems because both electrons and holes can readily participate in the redox reaction on their surfaces. Furthermore, one-dimensional (1D) nanostructures as photocatalyst substrates have been extensively used due to their unique structural and electronic properties and superior performances in the heterojunction systems. 1D nanostructures such as nanorods and nanowires/nanobelts possess several advantages as follows: large aspect ratios which can increase the capacity of light absorption; great separation efficiencies of photo-generated charge carriers due to their high mobility and straight transport pathways. In this work, we have fabricated SnO_2/ZnS nanocomposites of SnO_2 QDs (quantum dot)-deposited ZnS nanorods as 1D heterojunction nanostructures through a facile two-step hydrazine-assisted hydrothermal process without using any complex surface treatments to introduce new functional molecules or additional inter-connectivity. It is noteworthy that a rational synthesis of high-quality SnO_2/ZnS heterojunction nanocomposites via a simple and friendly manner has not been reported yet. The photocatalytic activity and photostability of SnO_2/ZnS heterojunction nanostructures are much higher than the respective ones of ZnS nanorods. The decay time, as well as the intensity, of the band-edge emission of SnO_2/ZnS nanocomposites decreases progressively and rapidly with the increase of the SnO_2 content, indicating that the higher photocatalytic degradation efficiencies of SnO_2/ZnS nanocomposites result mainly from the increased separation rates of photogenerated charges. Our prepared SnO_2/ZnS nanocomposites are considered to have great potential for photodegradation nanocatalysts in the field of waste-water treatment.

Solid State Electron Paramagnetic Resonance Spectroelectrochemistry to Probe Redox Activity in Porous Framework Materials

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Ranging from singular redox-active organic components to extended electro-active framework materials and including all the metal clusters in between, electron paramagnetic resonance (EPR) spectroscopy remains a primary technique for characterising unpaired electrons in various materials. As it is designed to characterise unpaired spins, this makes it a perfect technique for coupling with electrochemistry, whereby spectroscopy is performed in tandem with an applied potential resulting in *in situ* spectroelectrochemistry (SEC). One of the greatest advantages of *in situ* SEC lies in the inherent notion that various redox states are being accessed on the one sample, allowing a quantifiable comparison of spectroscopic data.

EPR SEC has already been reported as a technique in the solution state, through the application of a specifically designed sample cell featuring electrochemical components. In recent work by our group, this technique has been successfully modified to work in the solid state, specifically for probing the redox-active components of metal-organic frameworks. Vital information regarding the redox states accessed at different potentials were obtained, which also proved useful in elucidating the origin of various processes when correlated back to electrochemical data. This technique displays good potential compatibility with variable temperature setups, such as low temperature liquid N_2 variants, the application of which would increase the range of signals discernible.

Stabilising a reactive bacterial small molecule that activates T cells

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T cells (lymphocytes) are key mediators of our immune system. They are typically activated by peptides or lipid antigens (ligands). However, a newly characterised subset of T cells called MAIT (Mucuosal Associated Invariant T) cells are activated by small heterocyclic molecules derived from the bacterial biosynthesis of riboflavin (vitamin B2).[1] We discovered that 5-OP-RU, a ribityluracil analogue, is an extraordinarily potent antigen in activating MAIT cells (EC_{50} = 3.1 pM). However, this antigen is also very unstable in water ($t_{½}$ 88 mins, 37°C, pH 7.4), prone to degradative imine hydrolysis and intramolecular cyclisation. Herein we report the stabilisation of 5-OP-RU via a kinetically controlled synthesis, rationally designed by examining the mechanisms of its formation and degradation.[2] Using computer modelling to understand the conformational and structural basis of T cell activation, we then designed a water stable analogue and synthesised it in 10 steps from d-ribose. The compound was completely water stable and functionally equivalent to the natural product *in vitro* and *in vivo*.[2] We found a quantitative relationship between analogue potency and the predicted solution structure. The design, synthesis and immunological properties of these compounds will be described.

(1) Corbett, A. J.; Eckle, S. B. G.; Birkinshaw, R. W.; Liu, L. G.; Patel, O.; Mahony, J.; Chen, Z. J.; Reantragoon, R.; Meehan, B.; Cao, H. W.; Williamson, N. A.; Strugnell, R. A.; Van Sinderen, D.; Mak, J. Y. W.; Fairlie, D. P.; Kjer-Nielsen, L.; Rossjohn, J.; McCluskey, J. *Nature* **2014**, *509*, 361.

(2) Mak, J. Y. W.; Xu, W.; Reid, R. C.; Corbett, A. J.; Meehan, B. S.; Wang, H.; Chen, Z.; Rossjohn, J.; McCluskey, J.; Liu, L.; Fairlie, D. P. *Nat. Commun.* **2017**, *8*, 14599.

Starving Cancer Cells with Natural Products by Inhibiting ARTD8

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Natural Products have proven to be promising lead molecules for cancer therapeutics and many successful anticancer drugs are natural products or their structural analogues. Recent literature has highlighted the post-translational modification enzyme ADP-ribosyl transferase member 8 (ARTD8), also known as PARP14, as a potential therapeutic target. ARTD8 levels have been shown to be greatly increased in cancer cells in comparison to normal cells. ARTD8 has been shown to enhance cell survival through the activation of oncogenes, promotion of the Warburg effect, and making B cell lymphomagenesis more aggressive. It is possible that utilizing the genomic instability caused by inhibition of ARTD8 in conjunction with known cytotoxic chemotherapeutic agents that we may be able to target resistant cancers, such as, late stage prostate cancer. This study investigates a series of known natural product compounds as potential ARTD8 inhibitors through a combination of computational chemistry techniques and ARTD inhibitor assays to develop a novel target scaffold as a promising anticancer lead molecule.

Stereoselective Synthesis of Alkenylboron Compounds via Copper Catalyst

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Metal-catalyzed hydroboration of alkynes provides useful alkenylboron intermediates in synthetic chemistry. While the synthesis of (*E*)-alkenylboron via syn-addition is well-known, the synthesis of (*Z*)-alkenylboron via trans-addition is rarely reported.

In this presentation, we report ligand controlled stereodivergent hydroboration of terminal alkynes with 1,8-napthalenediaminatoborane. NHC-Cu catalyst producued (E)-alkenylboron compounds with high stereoselectivity up to >98% for various terminal alkynes. On the other hand, (Z)-alkenylboron compounds were produced in the presence of phosphine-Cu catalyst at mild conditions via trans-addition of the borane reagent.

Structural Investigation of Protein-DNA Interactions in Gene Switches Using Ion Mobility Mass Spectrometry

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Lambda and 186 bacteriophages, known as “gene switches”, are both models for understanding gene regulation as the lytic-lysogenic decision in bacteriophages depends on repressor proteins (such as the CI protein) bind to a DNA operator site. Although numerous studies have investigated these gene switches, some structural details of the protein-DNA interactions are still unclear. Here we developed a native mass spectrometry approach to probe these details.

Ion-mobility mass spectrometry (IM-MS) is a powerful and sensitive mass spectroscopic technique, which allows separation of ions based on both mass-to-charge ratio (m/z) and collision cross section (CCS), and is applicable to study of intact biomolecular assemblies in the native state. This research aims to detect the details of structures for lambda CI protein and 186 CI protein binding to various operators, such as OL_1, OL_2 DNA, via IM-MS experiments.

Our data shows the oligomerisation states of both lambda CI protein and 186 CI protein. Furthermore, the lambda CI protein binds to the OL_1 operator with pairwise cooperatively, such as dimer, tetramer and octamer stoichiometries, which is consistent with the reported results of repressor binding to long range DNA loops.

Study of Fatty Alcohol and Acid Assembly on Soil Surfaces

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ABSTRACT TEXT

Soil water repellency is a soil property that inhibits the infiltration of water through the soil profile. This results in different rates and degrees of wetting,[i] which can hinder plant growth and complicate crop and pasture management.[ii] Over two million hectares of southern Australia have been classified as water repellent,[iii] with estimated production losses surpassing $100 million.[iv] Previous research indicates that organic compounds found in soil acting as coatings on mineral grains,[v] or as particulate matter,[vi] are significant factors in causing soil water repellency. However, while speculative theories have been proposed to explain experimental data, little has been done to justify the theory at the molecular level.

Using molecular dynamics, models were created to simulate the organo-mineral interactions between hexadecanoic acid (PA) and hexadecanol (hexaOH) on sandy (quartz), weathered sand (amorphous silica) and clayey (kaolinite) soils (Figure 1).

Both PA and HexaOH equlibrate to a semi-parallel arrangement relative to the mineral surface. Concentration profile data suggests that the formation of organic molecule layers occurs on quartz and kaolinite at 1.0 molec/nm^2, whereas a third layer begins to form at 2.5 molec/nm^2.

Experimental studies involving the application of PA and docosanol (C_{22}) onto the surface of organic-free sand revealed increasing water repellency of the sand with PA/docosanol concentration. A speculative explanation of this observation is that increases in concentration of these organics creates a denser/thicker hydrophobic barrier due to the formation of multiple organic layers. Further work needs to be done to isolate the effects of mineral surface area and surface chemistry.

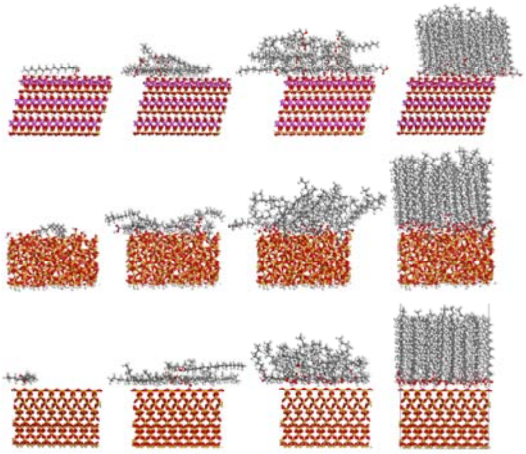

Figure 2: MD models of PA on kaolinite (top), silica (middle) and quartz (bottom) at different surface densities.

Study On CYP450 Family Based On Heterogeneous Information Networks

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ABSTRACT

Cytochrome CYP450 is a large family of enzymes that are widely present in animals, plants and microbes. They are closely related to the metabolism of most exogenous and endogenous compounds, and their functions are versatile, and also related to complicated multiple reaction mechanisms, so that all the objects related to the catalytic reaction, enzymes, substrates/drugs, reaction mechanisms, tissues/organs, and diseases compose an interacting heterogeneous network. In recent years, the newly developed heterogeneous information network in data mining has established a structural analysis for various types of objects and links, which puts forward corresponding solutions to the complexity and heterogeneity of information network. Therefore, we propose to study relationships among the individual enzyme and related objects in CYP450 catalytic reactions by the heterogeneous information network, so as to understand the CYP450 reaction mechanisms and the relationships between them. Based on the establishment of heterogeneous information networks some unknown drug metabolisms and catalytic reaction mechanism may be revealed.

SULFONATION OF TYROSINE-CONTAINING FC131 PEPTIDES FOR USE IN PET IMAGING

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Cell surface receptors overexpressed in cancerous tumours are feasible molecular targets for tumour imaging. The transmembrane G-protein coupled receptor CXCR4 is overexpressed and has a crucial role in organ specific metastasis of tumour cells. Cyclic pentapeptides such as the FC131 peptides have been developed to bind with high affinity and specificity towards CXCR4.
Through attachment of a positron emitting radionuclide such as fluorine-18, FC131 peptides have been previously investigated for use in positron emission tomography (PET) imaging of tumours. Despite the high binding affinity and specificity of FC131, its lipophilic nature results in high uptake in the liver. To increase hydrophilicity and promote favourable biodistribution, sulfonation of tyrosine residues in peptides has been investigated. Treatment of tyrosine with chlorosulfonic acid in TFA generates tyrosine-3-sulfonate, which is then incorporated into solid phase peptide synthesis of sulfonated FC131 peptide analogues. This work aims to compare the binding affinity and biodistribution of sulfonated FC131 peptide analogues to [^{68}Ga]-CPCR4-2, a current gold standard.

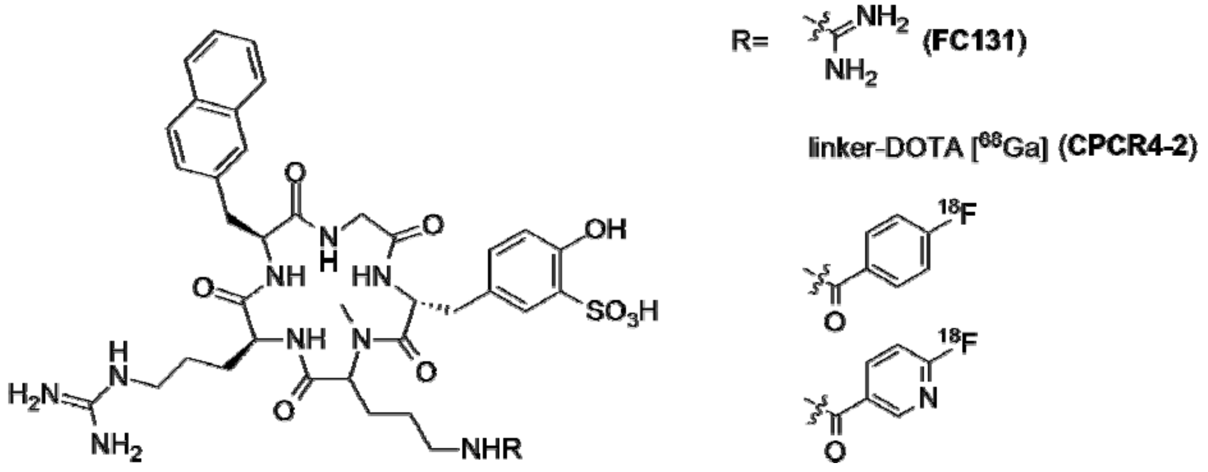

Figure 1: Sulfonated FC131 analogues

Super-resolution Imaging of silica coated metallic nanoparticles

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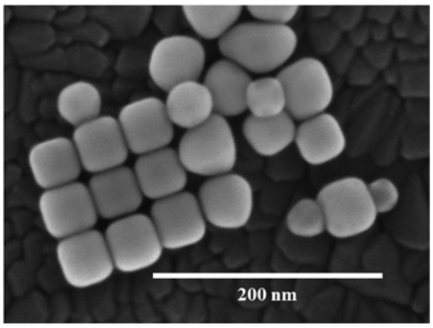
Metallic nanoparticles make interesting systems due to their variable properties compared to bulk materials. Gold nanoparticles have the capacity to adopt a variety of shapes, influencing the optical properties of these structures. Due to their size (2-100 nm), these particles are generally characterised by electron microscopy, with optical techniques being of limited use due to the diffraction limit of light (~200-300 nm). Super-resolution fluorescence microscopy techniques can bypass this limit, with single molecule based methods capable of achieving resolutions down to ~20 nm. We present single molecule super-resolution microscopy imaging of dye functionalised gold nanocube-silica layer samples. Nanocubes were synthesised using a pre-existing synthesis[7], with edge lengths of 40-45 nm. The silica layer thickness is tuneable and can be used to modify the distance between the attached dyes and the gold nanoparticle surface[8]. Correlation between electron microscopy and super-resolution fluorescence microscopy was performed, allowing accurate determination of the localisation precision of super-resolution fluorescence microscopy with respect to silica coated nanoparticle systems.



(a) *(b)* *(c)*

Figure 1: (a) shows a SEM image of 42 nm gold nanocubes, (b) shows the hybrid silica coated gold NPs labelled with fluorescent dyes, (c) shows a super-resolution microscopy image of a 40-45 nm nanocube with a 30-35 nm silica shell. The spot has a FWHM (full width at half maximum) of 104 nm.

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SYNERGISTIC OF Pseudomonas aeruginosa AND Pleurotus eryngii ON DDT BIODEGRADATION

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DDT is one of the organochlorine pesticides, which dangerous for environmental and human. Thus, it is needed method that can degrade DDT effectively. Biodegradation is environment-friendly method by using fungi and bacteria to degrade organic pollutants. In this study, the ability of white-rot fungus *Pleurotus eryngii* to degrade DDT was investigated as well as the effect of the addition of *Pseudomonas aeruginosa*. The addition of *P. aeruginosa* was variated at 1, 3, 5, 7, and 10 mL (1 mL ≈ 1,528 x 109 cells) into *P. eryngii* culture which incubated for 7 days. *P. eryngii* degraded DDT approximately 43.21%. *P. aeruginosa* culture at concentration of 7 mL was the highest DDT degradation approximately 90.20% among varied addition concentration. Mix *P. eryngii* and *P. aeruginosa* degraded DDT maximally at a concentration of 10 mL of 82.37%. Metabolic products resulting from the degradation of DDT by the mixture of *P. eryngii* and *P. aeruginosa* were DDD and DDE.

SYNTHESIS AND APPLICATION OF NOVEL ONE-HANDED HELICAL SUBSTITUED POLY(PHENYLACETYLENE)S

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ABSTRACT TEXT

A novel achiral phenylacetylene having an aldehyde group and two hydroxy groups was synthesized by deprotection reaction in membrane state of an one-handed helical poly(phenylacetylene) having dioxolane group by helix-sense-selective polymerization. The structures of the one-handed helical polymers and membranes were characterized by NMR, GPC, FTIR, UV and CD (Circular dichroism spectrum). The resulting polymer membranes showed good membrane forming ability which is very flexible. The enantioselectivity in permeation of the membranes from the resulting chiral polymers were examined. The polymer membranes having aldehyde group showed higher permeability and enantioselectivity than that of polymer membrane having dioxolane group in permeation of the racemate of phenylalanine (Phe). In addition, because of the introduction of aldehyde group, the permeability and enantioselectivity of the racemate of phenylethylamine of poly(phenylacetylene) membrane is much higher than that of the Phe. This result maybe cased by the reactivity between aldehyde group and chiral amine which mechanism is similar to the facilitated transport membrane. (157)

Synthesis and Application of a Self-Supported Polymeric Halogen Bond Donor

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ABSTRACT TEXT

Halogen bonds (XBs), which was defined by IUPAC as the non-covalent interactions between an electrophilic halogen substituent R-X and a Lewis base LB, have gained increasing attention since the mid-1990s, especially as catalysts in organic synthesis In this regard we have synthesized a self-supported polymeric XB donor functionalized with 2-iodobenzimidazolium groups. In the presence of 0.5 mol% of our polymeric XB donor, a variety of 2-arylquinolines were reduced to the corresponding tetrahydroquinolines with Hantzsch ester, and the catalyst was successfully recovered and reused several times. Aldimines were also successfully reduced with high yields. Our catalyst was then applied to Diels-Alder reactions of aldimines with Danishefsky’s diene. Finally, our catalyst was also successfully applied in Friedel-Crafts reactions.

SYNTHESIS AND BIOLUMINESCENCE OF HETEROCYCLIC ANALOGUES OF FIREFLY LUCIFERIN

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ABSTRACT TEXT

The several firefly luciferin analogues were synthesized by the solid-phase technique. Firefly luciferase catalyzes the oxidation of its substrate firefly luciferin (DLH_2) in the presence of oxygen, magnesium ion and adenosine triphosphate, resulting in the production of light. This light emission phenomenon, so called bioluminescence is widely utilized for biomedical research and drug development, such as *in vitro* cell based reporter gene assay and also for *in vivo* optical imaging. Recently, several synthetic luciferin analogues as new substrate for firefly luciferase have been reported. We also developed red-shifted luciferin analogues suitable for *in vivo* bioluminescence imaging. However, DLH_2 is a highly specific substrate for firefly luciferase, therefore, observed light outputs from modified luciferin analogues were commonly lower than those from native DLH_2. To investigate the light producing mechanism of luciferase and to obtain higher light output from modified luciferin substrates, several luciferin analogues were synthesized. The structure of DLH_2 consists with benzothiazole and thiazoline ring units. From our previous structure activity relationship study of synthetic luciferin analogues, thiazoline moiety was found to be the critical part to work as substrate. So in this study, benzothiazole moiety was substituted to heterocyclic structures, such as benzofuran, benzothiophene and indole. The protected cysteine bound resin was adopted for the solid-phase synthesis, and thiazoline ring was constructed *in situ* to obtain the target compounds. Compare to previous liquid phase synthesis of luciferin analogues in our lab, solid-phase method was suitable to obtain small scale products. Chemi-/bioluminescence property of synthesized luciferin analogues will be present.

Synthesis and characterization of Fe-Beta catalyst with high isomerization performance

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ABSTRACT TEXT

Conversion of vegetable oils into renewable hydrocarbon-based fuel can be achieved by catalytic hydrotreating to biodiesel products via decarboxylation or hydrodeoxygenation processes to obtain mainly *n*-alkanes. Furthermore, hydroisomerization of *n*-alkanes can be also significant depending on the characteristic of the catalysts and these reactions can contribute to upgrade the fuel properties that can be fed directly into unmodified engines because they are composed by hydrocarbons in the range of diesel and jet fuel [1, 2]. Metal/acid bifunctional catalysts, especially the Pt or Pd supported on zeolite molecular sieves showed good catalytic performance in hydroisomerization of *n*-alkanes, but the excess acidity of zeolites had been found to be responsible for the cracking of long carbon chains. Therefore, in this study a series of partially Fe-incorporated Beta-*x* (*x* was the ratio of $Al(NO_3)_3$/ $Fe(NO_3)_3$, x = 4.00, 1.50, 0.67, 0.25) zeolites were synthesized, and based on the Beta-*x* molecular sieve, a series of 0.5Pd/ Beta-*x* bifunctional catalysts were prepared. Their catalytic performance was investigated in *n*-hexadecane hydroisomerization using a fixed-bed flow reactor system. The highest *iso*-hexadecane yield of 69% was obtained at an *n*-hexadecane conversion of 82% over the 0.5Pd/Beta-1.50 catalyst, which can be attributed to the suitable amount and strength of the Brönsted acid sites.

Synthesis And Characterization Of Modified Urea Formaldehyde Resin

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ABSTRACT

Thermosetting polymer, urea formaldehyde resin is the most widely used adhesive for the production of wood based panels. Adhesive grade thermoformable Urea Formaldehyde (UF) resin has been synthesized in this piece of research work. To improve the mechanical properties of the synthesized UF resin, it was modified with thermoplastic polymer polyvinyl alcohol (PVA) during the reaction process. Optimum condition for the reaction was selected by changing the parameters such as time, temperature, pH, concentration of PVA and molar ratio of urea and formaldehyde. FT-IR spectroscopic analyses were done for synthesized UF resin and modified UF resin. Physical properties of both the liquid UF and modified UF resins were measured and reported. Polymer films of the synthesized UF resin and modified UF resin were made by solution casting method. Mechanical and thermal properties of both the unmodified and modified UF resin films were measured and studied to examine the effect on the amount of PVA incorporation in modified UF resin. Thermal properties of both UF resins exhibited almost the same glass transition temperature (Tg) and melting point (Tm) but improved tensile properties were obtained for modified UF resin than unmodified UF resin. The modified UF resin with 2% incorporation of PVA showed significantly higher tensile properties than other modified UF resins.

BODIPY-Based Profluorescent Probes Containing Meso and β Substituted Isoindoline Nitroxides

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ABSTRACT

Profluorescent nitroxides (PFNs) are a class of dual sensing redox/radical probes consisting of a fluorophore covalently tethered to a nitroxide moiety.[1] The nitroxide radical of a PFN quenches fluorescence by allowing relaxation through non-radiative electron exchange interactions and this fluorescence is revealed upon reduction or oxidation of the nitroxide or radical trapping. Whilst a number of different fluorophores have been incorporated into PFN molecules there is a distinct lack of long wavelength (>600 nm) emitting probes, limiting the potential for these probes to be used for deeply penetrative biological imaging applications such as near infrared (NIR) spectroscopy. A fluorophore which shows potential for such applications and has increased in popularity in recent years is boron dipyrromethene (BODIPY), which has a tuneable fluorescence emission in the range of 500-800nm.[2] In this presentation, the synthesis, optical properties and sensitivity of a range of novel BODIPY based PFN probes will be discussed and their potential as dual sensing redox/radical probes evaluated.[3]

1. Blinco, J.P., Fairfull-Smith, K.E., Morrow, B.J., Bottle, S.E., **2011**, *64*, 373-389.
2. Loudet, A., Burgess, K., **2007**, *107*, 4891-4932.
3. Allen, J.P., Pfrunder, M.C., McMurtrie, J.C., Bottle, S.E., Blinco, J.P., Fairfull-Smith, K.E., **2017**, 476-483.

Synthesis of Antihomoaromatic Mechanistic Probes for P450-catalysed Dehydrogenation

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The cytochromes P450 (P450s) are a large, catalytically diverse family of oxidative haemoproteins which play important roles in a variety of vital physiological processes across all kingdoms of life. Key oxidative transformations catalysed by these enzymes include hydroxylation and dehydrogenation, the latter of which is poorly understood, despite playing a significant role in drug metabolism in humans, and in the biosynthesis of steroids in plants and fungi.

To understand the mechanism of P450-mediated dehydrogenation, a model bacterial enzyme, CYP199A4, is being investigated. We aim to determine whether CYP199A4-catalysed dehydrogenation occurs directly via a radical intermediate, or whether a second electron is lost to form a cationic species before proton abstraction gives the desaturated product.

To distinguish between these hypothesised pathways we propose fused tricyclic system **1** as a probe substrate. It is expected to respond to the abstraction of a radical via cyclopropyl ring opening, and the formation of a cation generates an unstable antihomoaromatic system, which would effectively inhibit the dehydrogenation pathway and favour hydroxylation. Thus analysis of the product profile should indicate the presence or absence of a cationic intermediate. Compounds **2** and **3** were identified as potential controls for examining radical abstraction and cation formation in the absence of antihomoaromatic destabilisation. The synthesis towards the novel compounds **1**, **2** and **3** (Fig. 1) and preliminary physical data will be presented.

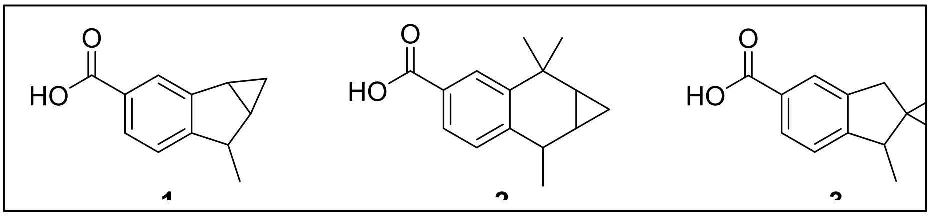

Figure 1. Mechanistic probe **1** and control substrates **2** & **3** for CYP199A4-catalysed dehydrogenation.

SYNTHESIS OF CHIRAL COVALENT ORGANIC FRAMEWORKS USING (+)-MENTHOL AS CHIRAL SOURCE

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ABSTRACT TEXT

Novel chiral covalent organic frameworks (CCOFs) having different size of pores were synthesized by using (+)-menthol as chiral source. Three kinds of linkages were used in the synthesis of CCOFs, such as, boroxine, alkynyl group and imines. The resulting CCOFs were characterized by infrared spectroscopy (IR), scanning electron microscope (SEM), transmission electron microscope (TEM), power X-ray diffraction (PXRD), circular dichroism (CD), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC) and Brunauer-Emmett-Teller (BET). The crystallinities and porosities of boroxine linked CCOFs were higher than that of linked by alkynyl group and imines. However, the stability of CCOFs having alkynyl group and imines as linkages were higher than that of boroxine linkage in the presence of water or protic solvents because of the decomposition of its boroxine bonds. The CCOFs were used as preliminary enantioseparation materials for 2-butanol racemate.

VISIBLE LIGHT PHOTOREDOX CASCADE CARBOARYLATION OF SUBSTITUTED *N*METHACRYLOYLBENZAMIDES FOR THE CONSTRUCTION OF ISOQUINOLINEDIONES

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Visible light photoredox catalysis has received considerable attention as a versatile strategy towards generating diverse organic radicals.[9] Owing to the broad and tuneable redox potentials of available photocatalysts, the generation of aryl and alkyl carbon-centred radicals proceeds under mild conditions without the need for stoichiometric radical initiators and toxic reagents often mandated by traditional approaches.[9]

As part of our interest in the discovery of catalytic radical reactions for the generation of novel aza-heterocycles, we have developed a radical cascade reaction mediated by visible light photoredox catalysis to generate a series of isoquinolinediones (Figure 1). The cascade reaction proceeds via the addition of an alkyl radical to *N*methacryloylbenzamides, generating a 3° radical intermediate that subsequently undergoes intramolecular homolytic aromatic substitution to give the isoquinolinedione products in good yields. The sequence is triggered by the formation of an alkyl radical via decarboxylation of active *N*-hydroxyphthalimide esters.[10] The reaction is amenable to primary, secondary and tertiary radical species and displays good substrate scope.

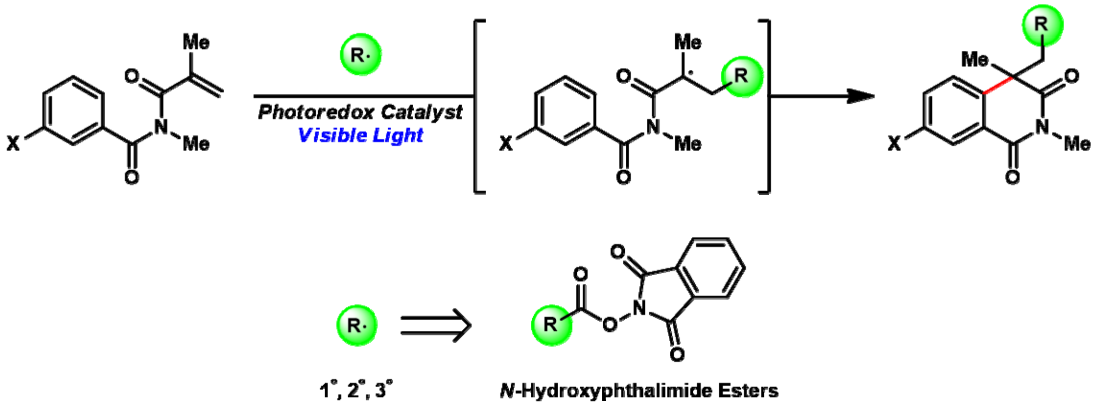

Figure 3. Catalytic cascade reaction to form isoquinolinediones.

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Synthesis of Metal Complexes of N-Heterocyclic Carbenes and Their Catalysis

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ABSTRACT The coordination and organometallic chemistry of *N*-Heterocyclic carbenes (NHCs) have been developed quickly, and NHCs have been widely used for the preparation of transition metal-based catalysts. Metal NHCs complexes have been found extensive applications in C-C and C-N formation reactions. Transition metal complexes of NHCs are normally obtained through reactions of free carbenes and corresponding metal salts, transmetallation of Ag-NHC complexes, or reactions of imidazolium salts with basic metal salts. We present more direct and convenient synthetic methodologies for the preparation of metal NHC complexes. A number of metal-NHC complexes have been obtained in moderate to excellent yields through reactions of commercially available metal powder with imidazolium salts. The copper and nickel NHC complexes were used as carbene transfer reagents for the preparation of other noble metal complexes such as palladium, platinum, and rhodium complexes. A few C-C and C-N formation reactions will also be presented by using these metal NHC complexes.

Synthesis of nano Zn-substituted ZSM-5 zeolites and their aromatization performance

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ABSTRACT TEXT

In today's society, the fuel consumption increased greatly with the rapid development of automotive transportation, as a sequence, exhaust pollution becomes more and more serious. In China, approximately 80% of gasoline comes from FCC processes in which the olefin content is usually as high as 45–65 vol.%. Therefore, it is crucial to decrease the olefins and sulfur contents in FCC gasoline. Many studies have shown that olefins aromatization is greatly favored over bifunctional Zn incorporated ZSM-5 zeolites[1].The incorporation method of isomorphous substitution effectively avoid the blocking of the micropore and the loss of active component compared with impregnation method. Moreover, microwave-irradiated heating (MW) provides distinct advantages such as rapid heating, homogeneous nucleation as well as a shorter crystallization time. Hence, this research was undertaken to study the influence of heating methods both conventional electric heating (CE) and microwave irradiation (MW) in the seed preparation and crystallization process of synthesis of nanosized ZnZSM-5 zeolite via organic structure-directing agent-free method on the physicochemical properties and catalytic performance in the 1-hexene aromatization. The results show that combine of microwave irradiation heating with conventional hydrothermal method can not only promote the nucleation and growth rate but also modulated the size and arrangement as well as the acid strength and density of the ZnZSM-5 nanocrystals. ZnNZ5-MW/CE sample exhibited the highest aromatics yield due to the intact micropore structure, higher concentration of Brønsted acid site as well as the promoted synergistic effect between Brønsted and Lewis acid sites.

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Synthesis of NiO/graphene nanosheets and their application in CO sensing

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ABSTRACT TEXT

Monitoring trace concentrations of harmful gaseous chemical species is increasingly needed in different areas such as indoor, outdoor, vehicle air control, mining and manufacturing sites. Hence, the fabrication of highly sensitive and selective chemical gas sensors are imperative. Chemi-resistive gas sensors based on semiconducting transition metal oxide are potential candidates due to their ease of operation, low cost of manufacturing, microscale miniaturization and good thermal and long-term stabilities 1–3. In this work, spherical NiO/graphene foam (GF) composite with nanosheets structures were successfully synthesized for their application as CO reducing gas sensor via a hydrothermal reflux process. X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and gas sorption analysis were used to characterize the structure and morphology of the samples. The results obtained from the SEM micrographs showed that the flowerlike NiO spheres successfully coated the entire surface area of the GF. The performance of the composite towards CO gas sensing was studied. The results reveal that the incorporation of graphene into flowerlike NiO spheres not only improved the conductivity and surface area of NiO/GF composite, but also enhanced the performance of the composite towards CO sensing. These results suggest that the composite could be a potential active material for CO reducing sensors.

Synthesis of novel 4-amidonaphthalimides and their applications

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Substituted naphthalimides are well documented in the literature for their use as dyes and fluorescent probes due to their high quantum yields and large stokes shift.[1] However synthesis of these molecules is often hindered by high temperatures, pressures, and stoichiometric amounts of expensive reagents.

The group at Deakin University has recently developed methodology for the synthesis of amine or amide-substituted naphthalimides using palladium-mediated cross-coupling reactions. This synthesis strategy allowed the rapid synthesis of substituted naphthalimides as fluorescent histone deacetylase (HDAC) inhibitors[2] – a target for anti-cancer treatment.

The nitrogen of both amine and amide substitutions on the naphthalimide ring are involved in internal charge transfer (ICT),[1,3] which leads to a highly fluorescent species suitable for fluorescent imaging studies. In addition, the unusual properties and sensitivity of the 4-amidonaphthalimides afford the potential for these compounds to be used in a range of applications such as anion sensors and cellular imaging agents (Figure 1).

Figure 1: Applications of 4-amidonaphthalimides

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Synthesis of Novel peroxisome proliferator-activated receptor δ agonists

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Peroxisome Proliferator-Activated Receptor δ (PPARδ) has recently come into the focus as a re-emerging drug target for the treatment of associated diseases such as metabolic syndrome as its activation alters glucose and lipid metabolism through a transcriptional regulation and results in beneficial pharmacological actions, typically an exercise mimic. We synthesized novel PPARδ ligands and an efficient synthetic route to these analogs was also developed. Surprisingly, some of compounds were potent and selective hPPARδ agonists with 200-fold selectivity over the other two subtypes, namely, hPPAR δ and hPPARδ. Some selective PPARδ ligands showed good bioavailability and in vivo efficacy. These results suggest that our novel PPAR δ agonists could be promising candidates for inflammation and metabolic diseases.

SYNTHESIS OF SUBSTRATE AND TRANSITION STATE MIMICS AS POTENTIAL INHIBITORS OF CYP121, AN ESSENTIAL ENZYME OF *MYCOBACTERIUM TUBERCULOSIS*.

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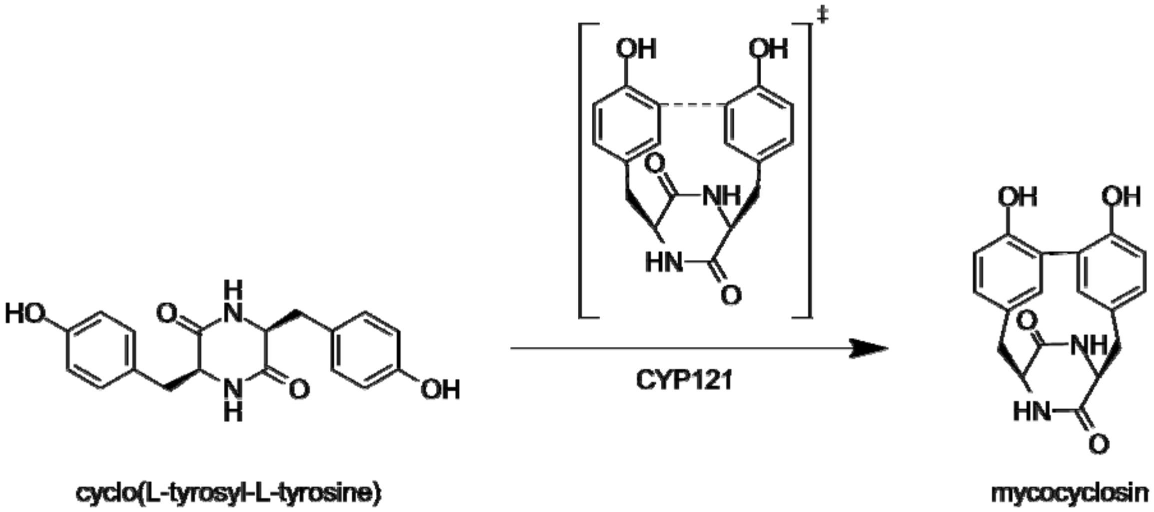
The growing incidence and degree of resistance exhibited by *Mycobacterium tuberculosis* to currently available treatments is of great significance. With multi- and total-drug resistant strains being reported alternative chemotherapies are required to overcome these developed resistances. A possible novel target of inhibition is CYP121, an essential cytochrome P450 enzyme of *Mycobacterium tuberculosis*.

CYP121 catalyses the formation of a secondary metabolite, mycocyclosin, from the cyclic dipeptide cyclo(L-tyrosyl-L-tyrosine). The design and synthesis of analogues of the CYP121 substrate and transition state, as potential inhibitors of the CYP121 enzyme, will be presented.



Synthesis of WEB-2086 Derivatives for the Treatment of Inflammatory Diseases Resulting from Respiratory Pathogens

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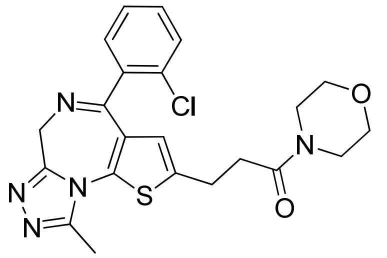
Bacterial infections of the respiratory tract by non-typeable *Haemophilus influenzae* (NTHi) and *Streptococcus pneumoniae* can cause life-threatening exacerbations for COPD (Chronic Obstructive Pulmonary Disease) patients.[1] It has been shown that these bacteria can bind directly to the PAFr, which is upregulated in the cells of smokers and COPD patients, thereby increasing the probability of an invasive bacterial infection occurring.[2] COPD is characterised by chronic inflammation and destruction of lung cells, due to an immune response. Current therapeutics focus on alleviation of the symptoms, rather than prevention. Early intervention is required to limit the incidence of infection, and thereby decrease the number of hospitalizations that occur as a result of bacterial exacerbation in COPD. It is known that antagonism of the PAFr can reduce the adhesion of NTHi and *Streptococcus pneumoniae* to bronchial epithelial cells, down to non-cigarette exposure control levels.[3] We have synthesised a library of antagonists based on the lead structure of WEB-2086, a well-known PAFr antagonist, and tested them for biological activity. The results of our research will be presented.



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Synthesis, photophysical and electrochemical properties of aza-boron-diquinomethene complexes

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Boron dipyrromethene (BODIPY) is the basis of an intriguing class of dyes that have been widely utilised in the area of molecular probes, photodynamic therapy, laser dyes, nonlinear optical materials and solar cells. Modification of BODIPY to form the aza-diquinomethene (aza-BODIQU) complexes provided complexes with new and interesting properties. Here, a series of aza-BODIQU complexes with different aryl-substituents (B1-B6, which are substituted with electron donating groups and electron withdrawing groups) were synthesized and characterized. Their photophysical properties were investigated systematically via spectroscopic and theoretical methods. All complexes exhibit strong $^1\pi$-π^* absorption bands and intense fluorescent emission bands in the visible spectral region at room temperature. The fluorescence spectra in solution show the mirror image features in the S_0-S_1 absorption bands, which can be assigned to the $^1\pi$-π^*/^{1}ICT (intramolecular charge transfer) emitting states. With the exception of the complex with a biphenylamine substituent for B6, all the other complexes exhibit high photoluminescence quantum yields (Φ_{PL}=0.47-0.93). The spectroscopic studies and theoretical calculations indicate that the photophysical properties of these aza-BODIQUs can be tuned by the appended aryl-substituents, which would be useful for rational design of boron-fluorine complexes with high emission quantum yield for organic light-emitting applications.

Synthetic Approach to Protein Organophosphorous Chemical Warfare Agent Bioadducts

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Organophosphorous nerve agents are very potent acetyl- and butyrylcholinesterase inhibitors and their development, production, stockpiling and use is prohibited by the Chemical Weapons Convention. Developed in the 1930s, nerve agent chemical weapons still pose a threat nowadays as recent events in Syria and Malaysia have shown. They react with biomolecules in the body and these bioadducts have an extended half-life compared to the unreacted, degraded and metabolized nerve agents in biological samples. This makes them very attractive as biomarkers, which can be detected using HPLC-MS/MS. Cholinesterase nerve agent adducts can age by losing the *P*-*O*-alkyl chain. The aged adduct is of special relevance since after a certain time it is the major marker found in biomedical samples.

In this work we successfully developed a method, based on a building block approach, to synthesize nonapeptide nerve agent adducts, which are relevant compounds for the analytical verification. Amino acids are phosphylated and further used in solid-phase peptide synthesis (SPPS). Additionally we developed and investigated two pathways for the synthesis of the aged adduct. Different protecting group strategies were used and an optimized SPPS protocol was developed which takes into account the lability of phosphylated amino acids. In the search for a purificationless preparation of the peptides we identified several side products and solutions to circumvent them were found.

The synthesized adducts can be used as reference standards in the search for evidence of exposure to nerve agents and are successfully in use in the development of biomedical analysis methods at Spiez Laboratory.

T-cell antigen formed from distinct metabolic pathways

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Mucosal associated invariant T-cells (MAIT cells)[1] form a large proportion of T lymphocytes in the blood (10%), liver (40%) and gut mucosa, yet there is still little information about them in textbooks. These lymphocytes appear to be important in antibacterial immune responses, but are also implicated in certain pathological processes such as inflammatory bowel disease. The identity of the naturally occurring antigen (ligand) was elusive until our recent discovery that a highly unstable molecule related to riboflavin (vitamin B2) is responsible for activating MAIT cells.[2] This antigen is formed *in vivo* through an imine-forming condensation of 5-amino-6-D-ribitylaminouracil (5-A-RU), an intermediate in the bacterial biosynthesis of riboflavin, with pyruvaldehyde, a glycolysis metabolite. Despite the antigen's tendency to undergo rapid degradative cyclisation, we used advanced MS and NMR techniques to identify this antigen as 5-(2-oxoethylideneamino)-6-D-ribitylaminouracil (5-OP-RU). Crystallography showed that this antigen forms a second imine covalent bond with the amine side chain of a lysine residue that is sheltered in the hydrophobic environment of the MHC-related protein 1 (MR1). This creates an unprecedented double Schiff base moiety. These findings show unexpected structures of T-cell antigens, arising from different metabolic pathways and using surprising mechanisms of antigen presentation.

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Temperature Dependent Crystal Structure of MoO_3 Anode for SIB use

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Secondary battery systems are considered as an essential energy storage system (ESS). Among them, rechargeable Li-ion battery (LIB) is recognized as the best one right now. Although, LIB has gained a huge success in small portable electronic devices and electric vehicles, they are not suitable for large-scale grid. Because Li which is the main material of LIB has limited supply as the Earth's crust runs out thus the cost of lithium is increasing. Sodium, the second lightest alkali metal, attracts researcher's interest as an alternative choice because of their potential advantages of low cost and the widespread availability of sodium resources. For large-scale energy storage systems, many great studies have made progress in exploring capable Na cathode. However, only a few anode systems have been investigated. Therefore, research work about favourable anode material is important in development of sodium-ion batteries (SIBs). As an anode material for SIBs, molybdenum-based materials were used because they have many advantages such as low cost, abundant resources and non-toxicity.

In this work, nanobelt and hexagonal prism structured MoO_3 were successfully synthesized by solvothermal method for SIB use. The structures of MoO_3 were dominantly influenced by the synthetic solvothermal temperature. This temperature also affects the crystallinity of MoO_3. Nanobelt and hexagonal prism structures were characterized by Scanning electron microscope (SEM), X-ray Diffraction (XRD), Energy dispersive X-ray spectroscopy (EDS). Electrochemical properties were measured by Cyclic Voltammetry (CV).

The “End” of Single Crystal Gold Nanorod Growth

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Shape control of nanocrystals is essential for designing functional structures and, therefore, specific properties. It is achieved via a complex interplay of kinetic and thermodynamic factors specific to a given colloidal synthesis. Single crystal gold nanorods are one of the archetypal morphologies for anisotropic nanocrystals. However, the mechanism via which they break symmetry and further grow is complex with many unanswered questions. We have shown that $AgNO_3$ concentration controls sizes at which symmetric gold seeds start growing only in two directions (break symmetry) and their subsequent aspect ratio[1,2]. Additionally, there have been mixed reports of the identity of the nanorod surface facets and it is clear that there is an evolution of the surface morphologies during the nanorod growth[3].

The nanorods continue to grow in the growth solution if not isolated after the first 2 hours of growth and, generally, at this time only around 15% of the initial gold precursor are incorporated into the gold nanorods[4,5]. Here, we investigate the growth of gold nanorods via a long continuous growth. The final product of the long-term growth can be thought of as the most thermodynamically stable nanorods under the solution conditions (although we qualify that it is a metastable state as these are colloids). We will present the evolution of size and shape, including evolution of the surface faceting and morphology, during this long-term growth. We observe very highly rounded nanorod morphologies in the final product. The effect of the $AgNO_3$ concentration on the final nanorods will be discussed.

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The Effect of Lewis Acids on Type I Photoinitiators

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Free radical polymerisation reactions are the dominant method of polymerisation in the modern world. An understanding of the kinetics of these systems has been obtained for many years using Pulsed Laser Polymerisation (PLP) and photoinitiator species with well-understood photochemical behaviour. In recent years, a great deal of hope has been placed into Lewis acids and their capacity to catalyse free radical polymerisation reactions while also potentially offering an avenue towards the holy grail of this method: stereocontrolled free radical polymerisations. Progress towards this goal has been slow however as experimental results remain very difficult to obtain due to a loss of PLP characteristics upon addition of a Lewis acid to the system. The difficulty results in unusual excitation behaviour of the photoinitiator, which we believe stems from interactions between the Lewis acid and the photoinitiator species.

This work examines the effects that complexing one of two common Lewis acids has on the photo excitation behaviour of two well studied photoinitiator species. It will discuss the resulting implications that this will have for PLP experiments, and also also offer a potential solution to problems encountered when conducting PLP on these systems.

The effects of intramolecular hydrogen bonding in unsymmetrical squaraines on photovoltaic performance

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Three unsymmetrical squaraines (USQs) with different number of hydroxyl groups (BIISQ bearing two hydroxyl substituents, BIISQ-MOH bearing mono-one, and BIISQ-NOH bearing none) have been synthesized for understanding of the molecular structure-property relationship of photovoltaic materials. Their solar cells based on BIISQ have obtained the best performance, which is approximately three times higher than that of BIISQ-NOH. Our research show that the introduction of strong intramolecular hydrogen bonding interactions in squaraines can affect the whole π-conjugated properties, such as deepening the HOMO energy level and thus enhancing the open-circuit voltage, increasing the dipole moment and then improving hole mobility, weakening the electron-withdrawing ability of centric four-membered rings (as A unit in squaraine molecule) and thus improving the compatibilities between USQs and PC71BM. This work reveals that the introduction of intramolecular HB interactions in π-conjugated systems could be a promising strategy in tailoring molecular properties, film morphology, and photovoltaic performance. Interestingly, our research also finds that when the molecular skeletons of donor materials are relatively similar, thin layer chromatography (TLC) analysis might be a simple, cheap, and rapid way to preliminarily forecast the compatibility between donor materials and PCBM.

The Fox-Herzberg System of C_2

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Using laser induced fluorescence techniques, we have systematically mapped out the $e^3\Pi_g \leftarrow a^3\Pi_u$ band system of C_2 known as the 'Fox-Herzberg' system. C_2 is one of the most ubiquitous molecules in the universe, and its spectroscopy is of particular interest in developing an understanding of the dynamics of comets, nebulae, carbon cycle stars and even hydrocarbon flames. We have performed extensive analysis of the rovibrational characteristics of the $e^3\Pi_g$ state up to v = 12, with levels higher than v = 4 being reported for the first time. Rotationally resolved spectra with rotational temperatures on the order of 60-100 K have been measured. Analysis of the low J lines that these spectra afford has allowed us to make a correction to the previously estimated magnitude of spin-orbit coupling in the $e^3\Pi_g$ state.

While C_2 has long been suspected of possessing pre-dissociative electronic states, no evidence has been discovered to support this. By probing vibrational structure in the $e^3\Pi_g$ state above and below the dissociation limit of the ground state $a^3\Pi_u$ (between v = 11 and v = 12), we believe we have found evidence that the $e^3\Pi_g$ state is in fact pre-dissociative, through J dependent lifetime shortening and an uncharacteristically sharp decrease in intensity. By incorporating a pre-dissociation mechanism into existing astrophysical spectral models, we are attempting to reconcile the disparity between observed and simulated statistical temperatures of interstellar C_2 spectra.

The Mechanism and the Kinetics of Thermal Decomposition of Gemcitabine

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Gemcitabine (GTB) is a nucleoside analog used in chemotherapy for various carcinomas. The thermal decomposition of GTB was measured with thermogravimetry, differential scanning calorimetry, and thermogravimetric analysis coupled with Fourier transform infrared spectroscopy. The IR spectra, high-performance liquid chromatography, and liquid chromatography-mass spectrometry of GTB and the residues of its thermal decomposition at various temperatures were determined. The molecular bond orders were calculated using an ab initio method from the GAMESS program of quantum chemistry. The mode of thermal decomposition for GTB was discussed. The kinetic parameters for thermal decomposition such as activation energy *E*a and the pre-exponential factor *A* were obtained using the Ozawa method. The prospective lifetime of GTB was estimated using the Dakin equation. The results indicated that the thermal decomposition of GTB is a three-step process and the first mass loss stage mainly is to lost furan ring. The initial decomposition temperature in either nitrogen or air is 225 °C. For decomposition in nitrogen, the *E*a and *A* for the initial thermal decomposition are 122.0 kJ mol^{-1} and 2.75 × 10^{10} min^{-1}, respectively. For decomposition in air, the corresponding *E*a and *A* are 133.8 kJ mol^{-1} and 4.37 × 10^{11} min^{-1}, respectively. The thermal stability of GTB is good under routine temperature.

The pathways of a drug binding to a GPCR

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G protein-coupled receptors (GPCRs) are huge pharmaceutical targets. Since the discovery of the first ligand bound GPCR crystal structure a decade ago, the structural information on GPCRs has steadily been growing. Through computational studies we now understand that GPCRs exist as a complicated ensemble of states, and it is important to appreciate that the drugs binding to them follow equally complicated behaviour.

We have conducted an extensive investigation of the binding of the antipsychotic haloperidol to the D_3R. Haloperidol has been in use for 70 years and despite a nasty side-effect profile is still a WHO essential medicine. GPCR targeting drugs are commonly plagued by side effects due to the high homology between receptors, especially in the orthosteric binding site. The leading approach to establishing selectivity in GPCR targeting drugs is to design them to bind outside of the orthosteric binding site, either bitopically or allosterically.

By using computational methods to examine the drug binding process in unprecedented detail, we can elucidate the drug binding pathways and identify metastable sites where the drug pauses on its way to the orthosteric site. These metastable sites are known to correlate well with allosteric sites and are promising areas to expand scaffolds into bitopic ligands. To accomplish this we have utilized Markov state models, a method that maps out binding pathways and estimates the kinetics of long timescale binding events by observing transitions in hundreds of shorter MD simulations.

The robustness of the HPLC-UV analytical method

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ABSTRACT

The robustness of HPLC-UV analytical method is one of the most important indicators for accurately and reliably measuring the active content in agricultural and veterinary chemicals.

There is generally a linear relationship between the peak area (S) in the chromatogram and the analyte's concentration (C) within the linear range:

$$S = \mathbf{R}\,C + b \qquad [1]$$

The slope, ***R,*** solely governs the robustness of the HPLC-UV method.

The peak area (S) can be obtained by integrating the peak area:

[2]

Where u is the measurement voltage (mv), which is detected using a photomultiplier, and has a linear relationship with the analyte's UV absorbance (A):

$$u=kA \qquad [3]$$

Where k is an instrumental constant, and A is dependent on the chemical's molar absorption coefficient ($\square$, L mol^{-1} cm^{-1}) at the particular wavelength, the flow cell path length (L, cm) and the solution concentration (c, mol L^{-1}), i.e.,

$$A=\square\cdot L\cdot c \qquad [4]$$

Eq [2] can be rewritten as:

[5]

Based on the modified Beer-Lambert law, Eq [5] can be rewritten as:

[6]

Where, F is volumetric flow rate (mL min^{-1}), N_0 is the moles of the analyte.

The slope ***R*** can be calculated as below:

[7]

Where V is the volume of the individual injection, and MW is the molecular weight of the analyte.

In summary, the **robustness** (***R***) of the HPLC-UV analytical method can be significantly enhanced by choosing a suitable UV wavelength at which the molar absorption coefficient ($\square$) is at the maximum.

The Shaping, Bending and Breaking of 1,2-phenylcyclobutylamine

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Understanding the conformational structure of a molecule is a key piece of information to determine the behaviour of a molecule in different environments. This is commonly investigated with the use of resonance enhanced multi photon ionisation (REMPI) techniques.

A gas phase spectroscopic analysis of the neurotransmitter 1,2-phenylcyclobutylamine (1,2-PCB) was undertaken. Multiple conformers were established with the assistance of ab initio calculations and barriers to conformational conversion were identified. Formation of one, two and three water clusters was observed, with electronic and vibrational spectra recorded.

It is often difficult to characterise vibrational aliphatic CH stretch regions and so computed spectra were treated to account for a crucial Fermi resonance involving a CH_2 bend overtone to produce spectra comparable to experimental data.

Photofragmentation of the 1,2-PCB cation resulted in vinylamine and styrene fragments. Additionally, an intermediate radical distonic ion was formed prior to fragmentation into vinylamine and styrene, resulting in a charge at the nitrogen atom and spin density on the aromatic ring.

The Synthesis and Characterisation of Graphene; Towards Nanofunctionalised Materials for Water Treatment Processes

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The availability of water is incredibly important as it plays a vital role in human civilisation and its growth and sustainability, both politically and socio-economically. However, accessing safe drinking water has become a global challenge due to large releases of industrial contaminants; heavy metals, pesticides, microorganisms, pathogens, pharmaceuticals with improper treatment. Carbon has a unique chemistry of purifying water, but prevailing carbon purification technologies are either cost-prohibitive or lack high efficiency. Here, graphene presents a novel and advanced approach that demonstrates characteristics towards efficient water treatment. Graphene is one atom thick and arranged in a honeycomb lattice of a 2-dimensional mesh and known as an ‘incredible’ material being thin, light, strong, hydrophobic, heat and electrically conductive. Graphene is usually produced from the oxidation of graphite flakes in an acidic medium known as a wet chemical solid state method, and where other methods used are; chemical vapour deposition, metal-organic chemical vapour deposition and mechanical exfoliation.

In this work, graphene is synthesised and characterised using a modified Hummer’s reaction. The graphene was then characterised for surface topography (pore size and structure) and wettability. The material is then intended for wastewater remediation studies as a future direction.

THEORETICAL INVESTIGATIONS OF BULK AND SURFACE PROPERTIES OF CHROMIUM CARBIDES

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ABSTRACT

Chromium carbides are used as a coating agent over metal surfaces due to their good wear resistance [1]. Chromium carbides exist in three stable phases, i.e. Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ [2]. We have used Density Functional theory (DFT) to compare the bulk properties of these phases of chromium carbides. The calculated cohesive energies and enthalpies of formation for Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ were found to be -37.074 eV, -70.838 eV, -195.607 eV and -0.846 eV, -1.307 eV, -1.871eV, respectively which are in good agreement with experimental results [3]. Further, we have studied the surface properties of different surfaces for Cr_3C_2. Based on the Surface Free Energies, Cr_3C_2 (111) surface has been found to be the most stable of all the calculated surfaces.

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TIN OXIDE GROWH MEASUREMENT AT INDOOR ENVIRONMENT

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We measured tin oxide growth rate at Indoor environment with electrochemical methods. Mainly used methods are Sequential Electrochemical Reduction Analysis (SERA) and Quarts Crystal Microbalance (QCM).

The surface oxide thickness affects tin soldering. This is because that the melting point of tin oxide is higher than that of tin itself. Since the oxide layer forms at indoor environment, engineer need to estimate the oxide thickness for better soldering. This work shows the tin oxide growth.

We obtained that two oxides SnO and SnO_2 are formed on the tin surface and found that SnO_2 grows at indoor environment.

Ti-Nb-Ta-Zr-O Nanotubes Arrays and Their Applications for PEC Water Splitting

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Introducing foreign elements into the crystal structure of TiO_2, which modifies the optical and electrical properties, is a promising approach to foster the application deployment of TiO_2. Nevertheless, the progress has been retarded by the difficulties of achieving uniform and homogeneous mixing of the foreign elements with TiO_2. By performing anodization on Ti-based alloys, uniform nanotubular arrays of mixed oxides can be obtained. With the nanotube backbone offering spatial decoupling of light absorption from carrier collection, this nanotubular array can find potential use for energy conversion applications such as PEC water splitting. This work reported a one-step anodization process for the preparation of quaternary mixed oxides nanotubes and demonstrated their utility in PEC water splitting. The synthesis was conducted by performing anodization on a flake of Ti-29Nb-13Ta-4.6Zr alloy at 60 V in the fluoride-containing electrolyte, which resulted in the self-organization of quaternary Ti-Nb-Ta-Zr-O nanotubes arrays (denoted as TNTZO). Further heat treatment led to the growth of crystalline structures in two primary phases, anatase and rutile. For the TNTZO, the composed Nb oxide can induce shallow donor states to increase the electron conductivity, while the introduced Zr and Ta oxides may cooperate with TiO_2 promoting effective charge separation. These attributes, together with the nanotubular architectures, make the present TNTZO an ideal photoanode candidate for conducting efficient water splitting. The current study demonstrated the first example of employing quaternary mixed oxides photoelectrodes in PEC system, which paves the way for their advanced use in various photoconversion processes.

Total synthesis of (±)-5-*epi*-taiwaniaquinone G

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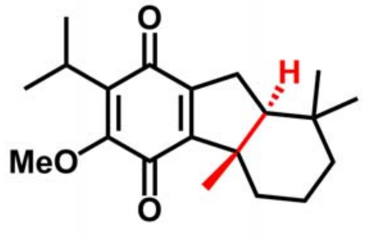
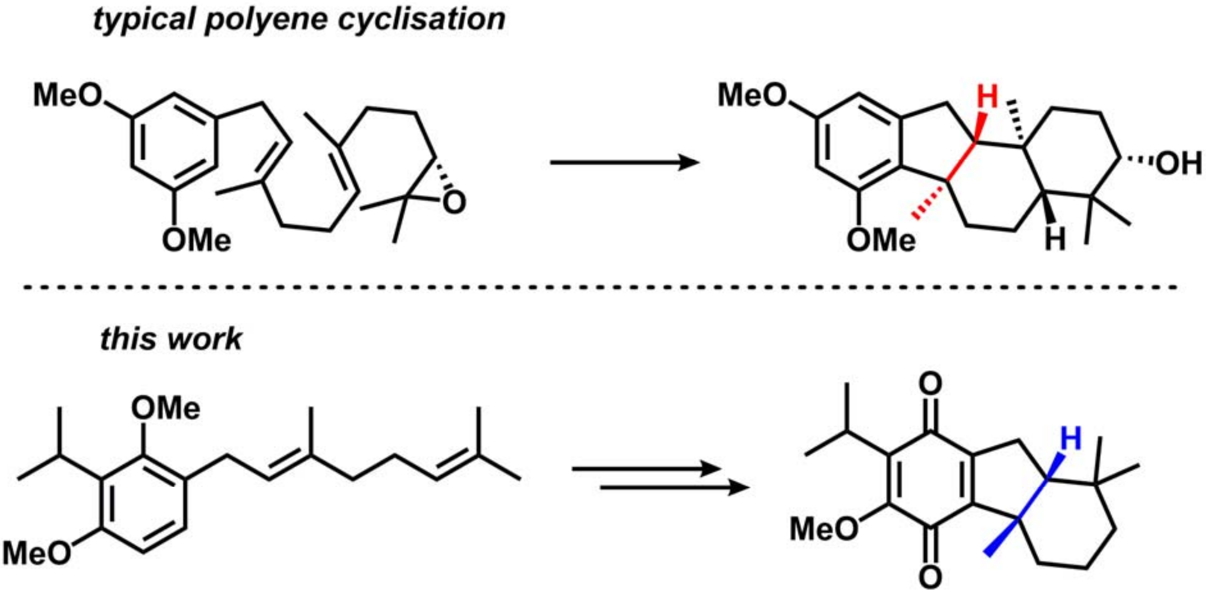
Since their isolation in 1995, the taiwaniaquinone diterpenes have attracted considerable synthetic attention. Taiwaniaquinone G represents an unusual member of the family; biosynthetic excision of a carbon atom has left it with a norditerpene skeleton, and its *trans*-fused ring junction contrasts with the *cis*-fused ring junction possessed by most of the taiwaniaquinone family. (−)-Taiwaniaquinone G has been synthesized twice before: In 2009 Alvarez-Manzaneda and co-workers reported a 14-step synthesis, using a chiral pool reagent to ensure the requisite *trans* stereochemistry; In 2012 they reported a biomimetically inspired synthesis of (−)-taiwaniaquinone G in 23 steps from (+)-abietic acid. The *cis*-configured epimer, (−)-5-*epi*-taiwaniaquinone G, has been synthesized on three occasions by hydrogenation of unsaturated precursors.



(-)-taiwaniaquinone G

In an attempt to improve the step economy of the synthesis, we sought to install the *trans*-fused 5,6-ring system directly by a cationic polyene cyclisation of a substituted geranylbenzene derivative. Despite reports of longer polyene and polyene epoxide systems undergoing cyclisations to give *trans*-fused 6,5,6,6- and steroidal frameworks, this particular cyclisation had not previously been reported. We are pleased to report the first such cyclisation, which unprecedentedly yielded the *cis*-fused epimer. This outcome enabled a short and efficient synthesis of (±)-5-*epi*-taiwaniaquinone G. Density functional theory calculations were carried out to determine the origin of this selectivity.


typical polyene cyclisation

this work

(±)-5-*epi*-taiwaniaquinone G

Tough hydrogel using crystalline nano cellulose grafted with acrylamide

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Several methodologies have been developed to produce robust and elastic gels. These include double network formation, use of clay reinforcement and cross-linked networks. These techniques have number of drawbacks, such as tedious sample preparation, use of special monomer requirements for the double networks and inability to use ionic monomers with nanoclays.

In this work we demonstrate that extremely tough and extensible gels can be produced through simple radical polymerization of any standard polymerizable monomer with nanocrystalline cellulose (CNC) as a crosslinker and reinforcement domain. The resulting nanocomposite hydrogels containing 85% water are extremely elastic and are shown to have high mechanical properties with an extension more than 4000 % with more than 250 kPa elongation strength. These gels have prolonged shelf life and can be constructed within a variable time frame (minutes to hours) according to the applications requirements.

In principal this is a very simple way of producing extremely robust and stretchy hydrogels that could be applicable to almost any monomer.

These hydrogels are suitable for developing highly absorbent hygiene products, as well as for applications in medicine, engineering materials and sensors.

TOUGHENING GELS FOR BIOMEDICAL APPLICATIONS

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Gels are used routinely in almost all biochemical and medical facilities, especially for the separation, analysis and purification of biomolecules such as proteins, DNA and RNA. Polyacrylamide gels are widely used for this purpose, but are fragile and easily torn. By the addition of a simple multi-armed cross-linker to existing formulations, we show it is possible to improve the toughness of the polyacrylamide gel enormously, while having minimal effect on its separation of biomolecules.

Towards automated NEXAFS collection on SXR at the Australian Synchrotron.

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ABSTRACT TEXT

The Soft X-Ray beamline at the Australian Synchrotron is in the process of developing a High Vacuum Automated Near Edge X-Ray Absorption Fine Structure (NEXAFS) chamber. To this end we have started developing automated methods for collecting NEXAFS data on our existing end station. This presentation will briefly describe the technique of NEXAFS and how it will be beneficial in many research scenarios. The presentation will also detail the latest automated procedures that we have implemented and tested on the beamline as well as what is yet to come. It is envisioned that many of the automated procedures that we are currently developing will be directly transferable to the new High Vacuum Automated NEXAFS chamber. An overview of how we foresee the new chamber can run will also be presented.

Transformation of Water-Soluble Drugs into Ionic Liquids and Lipophilic Salts For Enhanced Delivery Using Lipid Formulations

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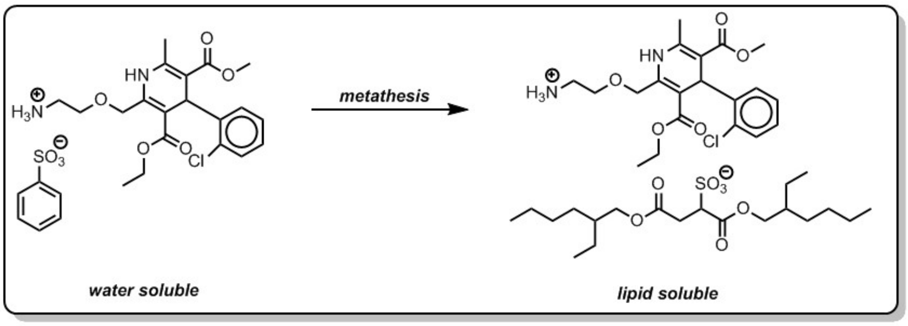
ABSTRACT

The higher lipid solubility of lipophilic salt forms creates new development opportunities for high dose liquid-filled capsules. The purpose of this study was to determine if lipophilic salts of the water-soluble drugs amlodipine, fexofenadine, ranitidine and metformin were better candidates for lipid formulation development than existing commercial salts. New lipophilic salts were successfully prepared from lipophilic anions and commercial HCl or besylate salt forms of the API via the metathesis reaction, confirmed by several analytical methods. Salt thermal properties were assessed by DSC and hot-stage microscopy. XRD and polarized light microscopy were used to confirm salt physical form. All lipophilic salt forms were substantially more soluble in lipidic excipients (typically >10-fold) when compared to commercial salts. For example, dissolved amlodipine concentrations in lipidic excipients were generally <5-10 mg/g when using the besylate salt whereas using the lipophilic docusate salt, >100 mg/g was achieved in at least 3 excipients. The higher lipid solubility of the lipophilic salts of each drug could be translated to higher drug loadings in lipid formulations. In vitro tests showed that lipophilic salts solubilized in a lipid formulations resulted in dispersion behaviour that was at least as rapid as the dissolution rates of conventional salts. This study highlights the applicability of forming lipophilic salts to facilitate the formulation of water-soluble compounds in lipid-based delivery systems.



Transition-Metal-Free Oxidation of Allylic Alcohols to α,β-Unsaturated Carboxylic Acids

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ABSTRACT

Green chemistry, also known as sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. From the perspective of green chemistry, we recently addressed our efforts to the design and development of transition-metal-free oxidation using $NaO^{t}Bu$-O_2 system. As a result, allylic alcohol can be readily converted to the corresponding α,β-unsaturated carboxylic acid under mild conditions. The present protocol is an eco-friendly alternative to a conventional transition metal-based method. This new strategy allows large-scale production with non-chromatographic purification, while also suppressing competitive reaction pathway.

Triplet Recombination in Singlet Fission

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In the search for more efficient solar energy harvesting, many processes are being investigated on the basis that they can generate multiple excitons from one absorbed photon. One type of multiple exciton generation (MEG) is singlet fission (SF) which takes place in aromatic hydrocarbons. An ideal scenario could allow single threshold solar devices to increase efficiency from 33% to 46% under AM1.5G spectrum (air mass 1.5 global), by utilising the singlet fission process (Tayebjee, 2012). However, the underlying mechanisms are not fully understood for the wide spectrum of molecules that undergo this process. With this poster, I will detail the theory behind the process of singlet fission and the experimentation being done to support it. This includes fast time and spectrally resolved spectroscopy, as a primary method to elucidate kinetics, and as a pathway for integration of observations into theoretical models based on bi-molecular reaction kinetics.

Tayebjee, M. J. Y., A. A. Gray-Weale and T. W. Schmidt (2012). "Thermodynamic Limit of Exciton Fission Solar Cell Efficiency." The Journal of Physical Chemistry Letters **3**(19): 2749-2754.

UNDERSTANDING COMPETING PHOTOCONVERSION KINETICS IN PRINTABLE NANOPARTICULATE SOLAR CELLS

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ABSTRACT:

Organic electronic devices fashioned from highly controlled polymer nanoparticle building blocks have received intense interest due to the ability to control the morphology and therefore function of the electroactive materials throughout the device fabrication process. However, organic photovoltaic devices produced using this nanoparticle approach (NP-OPVs) exhibit a low power conversion efficiency in comparison to the analogous bulk solution-based technology. Here, we report a systematic characterisation of the kinetics of various photoconversion mechanisms in nanoparticulate OPVs prepared using poly(3-hexylthiophene) (P3HT) as a donor and phenyl C_{61} butyric acid methylester (PCBM) as an acceptor material. Optical modelling analysis of the nanoparticle active layer morphology implies no significant losses in the internal absorption of NP active layers compared to bulk heterojunction reference devices. The internal quantum efficiency (IQE) of NP devices exhibited values of 25% in comparison to 76% for bulk heterojunction. Photoluminescence measurements confirmed exciton dissociation yields of 25% for NP devices in comparison to 81% for the bulk heterojunction, in excellent agreement with IQE results. Transient measurements of charge transport and bimolecular recombination rates confirmed a charge carrier drift length longer than the film thickness at short circuit conditions for both device structures. These results collectively explained that the main loss mechanism in the nanoparticle devices is poor charge generation arising from the core-shell morphology created during nanoparticle fabrication.

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Understanding the Primary Oxidation of Terpenes

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The oxidation of isoprene, initiated primarily by the hydroxyl radical, is the predominant source of secondary organic aerosol. (Ghosh, 2010) In pristine forested regions containing high isoprene concentration, the modelling of this process underestimates the steady state concentration of the hydroxyl radical by more than an order of magnitude. (Whalley, 2014) This sizeable discrepancy stems from an incomplete chemical understanding of this oxidation process and those that follow.

The hydroxyl radical is most susceptible to add across one of the double bonds of isoprene, forming a hydroxyisoprenyl radical. The most favourable addition products are those that yield resonantly stabilised intermediates, containing allylic radical motifs, as seen in figure 1. Building upon work by Gasser (2010) on the excited states of allyl and methyl allyl systems we continue adding methyl and hydroxyl substituents to these allylic frameworks in a ground up approach. The addition of OH to isoprene yields 6 different isomers, making the spectroscopy difficult. Intelligent precursor design allows us to study each isomer individually, reducing the complexity of the analysis.

Experiments will be conducted on the vibrational and vibronic transitions of these radicals in the coming months, both at NCTU, Taiwan and UNSW, and we hope to report on our findings at this conference. These results represent the first direct measurement of radicals produced from the OH addition to isoprene.

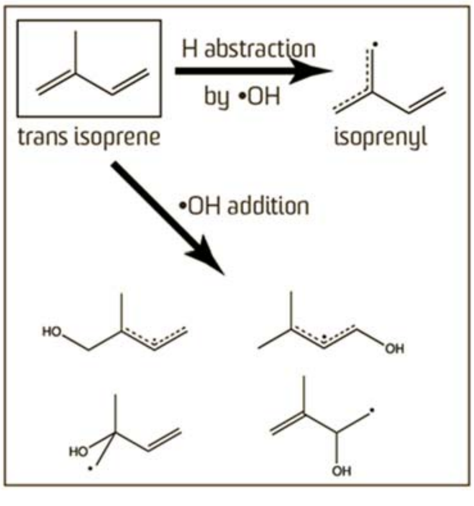

Figure 4. Hydroxyl initiated oxidation of isoprene

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University Chemistry Workplace Learning in Australia

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Compared to Europe, Workplace Learning (WPL) in Chemistry degrees in Australia is at its infancy. Edwards et al. (2015) report some disciplines in Australia – e.g. Health Science, Engineering, and Teaching/Education - have a history of WPL practices; however, Chemistry does not seem to have such a tradition. As such, this creates challenges for Universities and for workplace supervisors.

This talk will present the methodology for a project to assess the current state of WPL in Chemistry in Australian Universities. What are current practices of WPL in Chemistry degrees? What are the challenges? What are the best practices of WPL in Chemistry?

All Australian Universities offering chemistry degrees will be surveyed, determining details of Chemistry WPL experiences such as: graduate numbers; is there WPL in the degree?; compulsory or optional?; contained in a subject?; credit value?; student time requirement?; assessment?

Workplace supervisors will also be surveyed to investigate themes including: workplace motivations to host WPL students; expectations of WPL students; time for mentoring/training, and assessment of student's WPL?

Once WPL requirements at the institutions and employers are determined, data analysis will be conducted to identify common requirements and practices. Further conversations with WPL coordinators at surveyed institutions may be necessary to clarify issues and lead to a paper that could change perceptions in Australia about Chemistry WPL practices and how to improve assessment of students' WPL work.

Edwards et al. (2015) Work Integrated Learning in STEM in Australian Universities. Canberra: Office of Chief Scientist & Australian Council for Educational Research.

Unlocking Nature’s Treasure Trove of Medicines With an Espresso Machine

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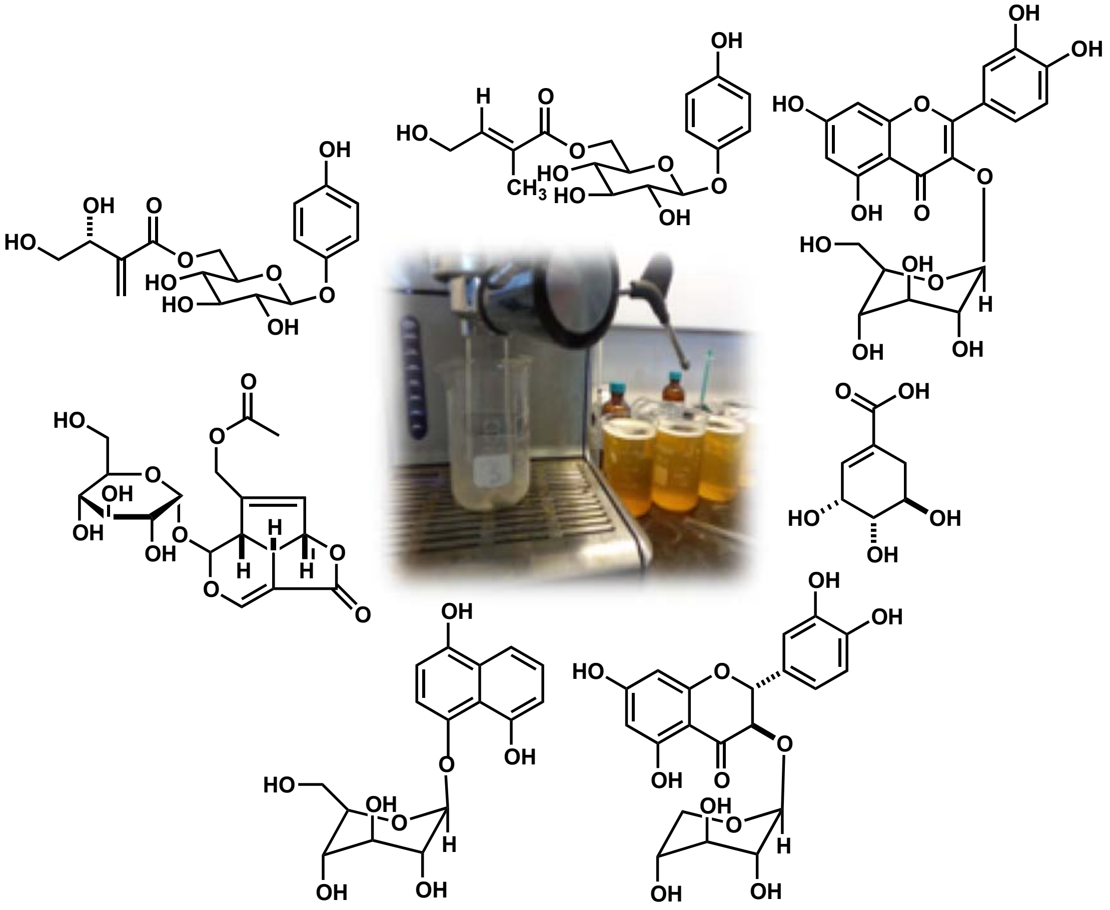
Our work has previously focused on the development of a method for the rapid pressurised hot water extraction (PHWE) of organic materials from plants using an unmodified household espresso machine. The PHWE screening method is a rapid technique for identifying the main chemical constituents of a plant, for applications in medicinal and synthetic chemistry. We have recently applied this PHWE method to survey a range of Tasmanian native and endemic plant species, to screen for potentially useful or novel organic molecules, and to determine chemical fingerprints for these species. Previous chemical investigations towards Tasmanian endemic plants have been limited, with natural products isolated from less than 5 % of species to date. The results of this study to date will be presented.



UTILISING COMPUTATIONAL MODELLING TECHNIQUES TO ENHANCE TERATOGENICITY DETECTION

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A teratogen is an agent which is capable of inducing birth defects in an embryo. It is desirable to identify potential teratogens early in the drug discovery process to gain insight into the toxicity profile of the drug under investigation. Therefore, the main aim of this project is to utilise ligand- and structure-based modelling methods to create *in silico* models capable of assessing drug teratogenicity.

The significance of this project lies in the possibility of detecting potentially teratogenic molecules early in the drug discovery process and to provide guidance for any toxicity testing which may need to occur. A database of Australian-approved drugs and their corresponding safety classification concerning their usage during pregnancy has been compiled. This database provides ligands of interest, which are broadly classified as: teratogens, non-teratogens and potential teratogens.

Methods used will consist of: Ligand-based methods which include database filtering (to enrich the database), overlaying chemical structures (to assess drug similarity) and molecular fingerprints (to categorise ligand structure and features to measure drug similarity). The structure-based methods focus on docking ligands to biological targets which are known to be involved in teratogenic pathways. The work presented here will showcase preliminary efforts in creating a suite of *in silico* models which may be employed to identify drugs with an elevated risk of teratogenicity.

VERSATILE SYNTHESIS OF 6-SUBSTITUTED PHENANTHRIDINES USING GOLD PHOTOREDOX CATALYSIS

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The phenanthridine core is an important scaffold in biologically active compounds frequently studied in medicinal chemistry. These scaffolds also find broad applicability in industrial settings such as dyestuffs. With recently increased research focus, several radical-based synthetic routes to functionalized phenanthridines have been developed. However, such methodology is restricted to the electron deficient coupling partners or highly activated substrates. The synthesis of phenanthridines using a 2-isocyanobiphenyl building block has been well studied as the isocyanide functional group is an excellent radical acceptor for both electron deficient and rich radical coupling partners. The radical addition and subsequent cyclization are highly reliable steps, leaving the greatest challenge in the facile generation of diverse and highly reactive radical intermediates. Frequently, these radicals have been generated using radical initiators such as azobisisobutyronitrile (AIBN), hazardous organostannanes, explosive aryl diazonium salts, and use of excessively halogenated alkyl substituents. While these strategies are effective, they strictly limit the scope of radicals that can be generated. The Barriault lab has developed a simple, mild and efficient method to generate radicals from unactivated bromoalkanes using gold photoredox catalysis. Bromoalkanes are commercially available and commonplace in most organic chemistry labs, generally stable for long-term storage. The use of bromoalkanes has allowed access to a diverse substrate scope previously unavailable through any other methodology, without sacrificing yields or employing harsh reaction conditions. This broadly applicable methodology tolerates a wide range of substituted phenanthridines in good to excellent yields.

Visible Light Photoredox Catalysis: Access to Novel Fused Ring Aza-Heterocycles

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Fused ring aza-heterocycles are highly represented in biologically active compounds however the synthesis of novel derivatives with unconventional substitution patterns is a challenge in modern synthetic organic, and medicinal chemistry. Classical approaches (Bischler-Napieralski and Pictet-Spengler reactions) mandate an electron rich aromatic system and high temperatures to promote electrophilic ring closure.

We report the development of a radical Pictet-Spengler reaction which ameliorates the electronic limitation of the polar reaction pathway. Our methodology involves the intramolecular cyclisation of carbon-centred aryl radical generated from the reduction of aryl iodides under photoredox catalysis[11,12] (Figure 1) to tethered aldimine and ketimine derivatives. This methodology has paved the way for the generation of novel tetrahydroisoqinolines under mild conditions using only photocatalyst (e.g. Ir(ppy)$_3$) and blue LEDs light. This radical Pictet-Spengler reaction can be readily extended to acess an array of novel fused-ring aza-heterocycles.

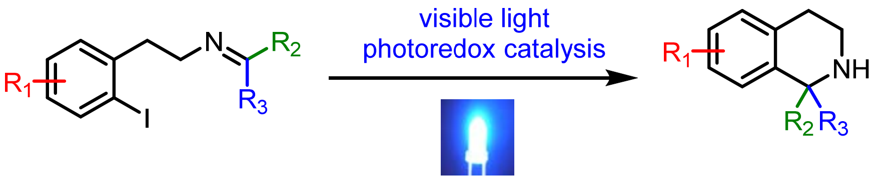

Figure 1.

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WHY PATENT?

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Factors to be considered when deciding whether to protect an invention include:

- Is it financially beneficial to patent? This may include consideration of which countries are most profitable to patent in and other strategic issues. Other considerations include whether the likely scope of protection and consequent potential revenue warrant the cost of obtaining a patent.
- Does the invention represent patentable subject matter? Patents are intended to protect technical subject matter. Areas where this becomes clouded include computer based inventions and business method inventions. This consideration may be different in different jurisdictions.
- Are there better ways to protect the invention? In particular instances there may be other suitable ways to protect an invention, including plant breeder's rights, circuit layout protection or maintaining a trade secret.

These factors should be considered on a case-by-case basis in order to ensure that a patent portfolio represents a beneficial return on investment.

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What happens when we do not have staff technically competent in chemical regulation and understanding of Chemical Safety issues?

Neale Jackson

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This paper presents looks at incidents and accidents that have resulted from the lack of technically competent staff to deal with chemical safety in a workplace. The results can be catastrophic to both the workplace and to the individuals involved if the wrong decision making process is undertaken. This paper will look at a decision tree analysis to show in two cases how at a critical stage if a different decision had been made that disaster would not have ensued.

This paper then further considers how over the past 10 years a situation has developed in which many courses/programs that specialise in the areas of Chemical safety and Toxicology have been disestablished to be replaced with more generalist type courses/programs and as a result there is the lack of ability to gain the important specialist knowledge required to avert disasters. The reasons for this will be discussed in terms of the priorities of specific professional organisations eg Safety Institute of Australia and their program accreditation process.

Given these circumstances there has developed a real concern with respect to where the specialists chemical and process safety personel of the future will come from. There is a perception amongst many of the current specialists that once they retire there will be no one around to fill this important gap.

- Lack of courses
- Lack of information
- SIA espouse a generalist perspective, very fragmented profession, identifying experts in different areas is very difficult
- Retiring consultants, loss of knowledge
- Lack of promotion aa a career option,
- HSE Div of RACI only 5 years old, gathering of some professionals, lots of work to do,
- IDG driven by individual professionals
- OHS Courses generic, not specialists, exception of what some specialist programs actually offer,
- Not many with a focus on Chemicals or DG
- Do other courses cover this type of content? Toxicology, but where have those courses actually gone,
- Impact, regulators, Industry
- How difficult to write SDSs how much information is actually required, can this be linked to disasters if not enough expertise is available to avert these things

CASE STUDY Artificial Turf – Environmental Friend, Health and Safety Foe?

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Artificial turf was first used in 1964. It has gone from being the domain of large professional playing fields to invading domestic lawns, public parks and gardens in search of a low water, low maintenance and aesthetically pleasing alternative to natural lawn.

Has the time poor, environmentally conscious householder been duped by shrewd marketing strategies? It has even been suggested that artificial turf will absolve one from legislated health and safety responsibilities. Questions have been raised as to potentially abnormal incidents of cancer in sports people who regularly play on artificial turf with a granulated rubber infill

In the quest for that perfectly manicured green lawn, has the consumer been deceived about the environmental impact that continue to shadow artificial turf? Environmental issues can be identified at each stage of the product lifecycle, making artificial turf less environmentally friendly than natural lawn.

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The European Chemical Agency's 2017 report on the possible health effects of recycled rubber infill, provides little more than generalised statements on the matter, and a list of uncertainties in its evaluation of granulated rubber. The United States EPA initiated its own multi-agency review into granulated rubber infill in 2016. In Australia and Hong Kong, the focus is on the potential of thermal burns and heat stress due to the heat generated by artificial turf and rubber infill.

This paper provides an update of current research of the potential health and safety issues of artificial turf.

Case study: Ceramic Non-stick Development

Christopher Phillips
The Cookware Company

Here we map recent developments in non-stick coatings and identify challenges for progression of “green chemistry trends” into the future.

Conventional non-stick was introduced ca. 1958. Since then, the basic fluoropolymer component has remained unchanged except for strengthening by using multiple layers and reinforcement materials. To this day, however, the maximum use temperature of fluoropolymers remains at 260^0C and, if accidentally overheated, degradation may occur. Yet consumers who preferred non-stick convenience were offered little choice in coating type until 2007 when Ceramic Non-stick (Sol-Gel) became more widely available.

Recently, environmental concerns surrounding PFAS’s (perfluoroalkyl and polyfluoroalkyl substances), which are commonly used in manufacturing various consumer products, led to 100’s of scientists to sign the Madrid Statement, which encourages adoption of alternatives to PFAS’s. This has coincided with growing public concerns regarding some of the PFAS’s used in making fluoropolymer dispersions. However, replacement processing aids for fluoropolymer dispersions generally have similar environmental problems. Only by changing direction (e.g. to Sol-Gels) is a non-fluorinated solution possible.

From 2007, some cookware manufacturers started offering Sol-Gel, which affords higher heat resistance without use of fluorinated raw materials or processing aids. Consequently, purchasing habits are evolving. A recent consumer surveys indicates that 52.3% of Americans are now likely to purchase Ceramic Non-stick with their ultimate decision being largely influenced by the non-stick longevity. Although the durability of Sol-Gels has significantly improved since 2007, continuing the progress will be the next chemistry challenge with only the most innovative manufacturers capitalizing on this green chemistry trend.

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