School of Chemistry

Honours Projects for 2013

MONASH University
Science

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INTRODUCTION - Honours 2013

This booklet is intended to provide an overview of the research activities within the School of Chemistry and to give you an indication of the Honours projects that will be offered in 2013. You are encouraged to study these and to speak with the research supervisors. This research project makes up 75% of the final mark for the Honours year, with the other 25% from the coursework component which runs in first semester.

Current third year students are eligible to do Chemistry Honours (Clayton) in 2013 provided that they fulfil the entry requirements and that a supervisor is available. Students will be allocated to supervisors and projects on the basis of their third year results and their preferred projects. Great care is taken to ensure that all students are treated equitably and where possible that they are be allocated to the area and supervisor of their choice.

All Honours candidates must discuss prospective projects with at least four supervisors before choosing their preferred project. They should then select at least three potential supervisors and projects in order of preference. The application forms – one for Honours entry which is from the Faculty of Science, the other is the project nomination form which is from the School of Chemistry – are both available on the School of Chemistry web page.

Please note that the project descriptions are quite short, and more comprehensive details can be obtained when speaking to supervisors.

We look forward to seeing you in the Honours course next year. Please contact me if you have any questions about the Honours year!

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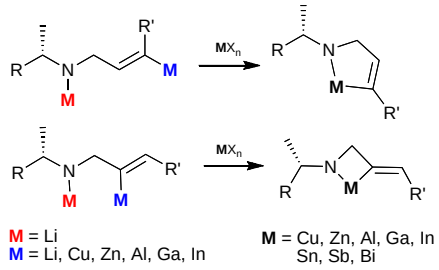
Targeting Novel Chiral Heterobimetallic and Metallocyclic Complexes

S-block organometallic complexes are key components of heterobimetallic complexes: in 'ate'-type complexes, *eg* cuprates, they allow regioselective conjugate addition reactions and in 'superbases' they support the regiospecific deprotonation of extremely weakly acidic protons, allowing electrophilic addition at normally inaccessible sites. Typically these complexes, *eg* $[BuLi.KO^tBu]_n$, are composed of two different anions and two different Group 1 metals.

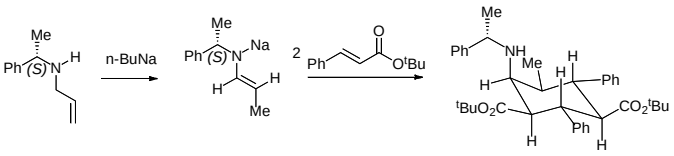


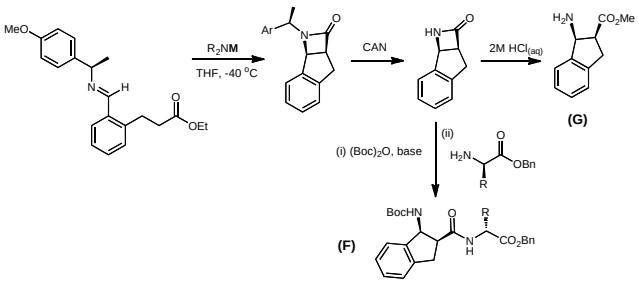
We have previously synthesized a series of novel chiral heterodianionic complexes through dimetallation of chiral allylamines; combining -N-Li and -C=C(H)M (M = Li, Na, K) moieties in a **single chiral dianion**. This established a novel family of heterobimetallic complexes with the core features of 'superbases' and '-ate' complexes.

The first part of this project will investigate the synthesis and full characterization of novel chiral heterodianionic and heterobimetallic complexes of alkali metal and d and p-block elements (Zn, Cu, Al, Ga, In, Sn, Sb). The second part will utilise dilithiated chiral allylamides as precursors to a new and unique family of chiral heterodianionic metallocycles. The reactivity and selectivity of these complexes is largely an unknown quantity. One fascinating feature that will impact immediately on reactivity and selectivity is that the individual N-M and C-M bonds will behave differently towards electrophiles. The project will involve the synthesis and characterization of the bimetallic and metallocyclic complexes and an assessment of their potential in asymmetric synthesis through reactions with prochiral substrates.

Chiral Metal Amides in Asymmetric Cyclisation Reactions

Chiral lithium amides, $[R_2^*NLi]$, are important reagents and intermediates in asymmetric synthesis, particularly for biologically active β-amino acids and β-lactams. To fully understand their selectivity and reactivity we have been investigating the structures the alkali metal complexes adopt both in solution and in the solid state. From these studies we have discovered that many complexes, particularly those of the heavier alkali metals (Na, K), can undergo anion rearrangements leading to new chiral complexes with differing reactivity, or even to a loss of chirality altogether. The amide to aza-allyl rearrangement shown as the first step in the Scheme has provided us with the basis for one of the most remarkable and exciting results to come from this chemistry. The enantiomerically pure aminocyclohexane is formed in a one-pot reaction, and contains **six** *new* vicinal stereogenic centres, formed through a highly stereoselective series of tandem aza-allyl conjugate addition – Michael addition – ring closure reactions.





Remarkably, reports of intramolecular ring-closure of enolates onto imines (*cf* - the last step of the cascade reaction) are virtually unprecedented. We have carried out preliminary investigations into the potential of this type of cyclisation reaction and found that it is facile, affording a highly stereoselective tandem route to extremely useful *N*-protected ®-lactams in very high de. This project will investigate the scope and limitation of this high impacting methodology for the asymmetric synthesis of ®-lactams/®-amino acids.

Bismuth-Precursors for Antimicrobial Organic-Inorganic Hybrid Materials

There is a steady and significant increase in microbial resistance to common antibiotics, and in fact many bacteria are now multi-drug resistant, for example *Staphylococcus aureus, Klebsiella pneumoniae and Pseudomonas aeruginosa*. This is primarily of great concern in medical and healthcare environments where it impacts directly on human health. However, it also demands the continual development of effective bactericidal compounds capable of combating increasing antibiotic resistance.

Bismuth(III) compounds show good antimicrobial activity, and are of low systemic toxicity in humans. This has led to increasing interest in bismuth and its potential applications in materials, medicine and bio-protective surfaces. Because of the way bacteria develop resistance, through mutation and evolution, it is easier for them to adapt to fully organic molecules than to those based on metals. There is no simple mechanism by which organisms can develop resistance to metal complexes. As such, there is great potential in the development of metal based antibiotics for both chemotherapeutic purposes and in generating 'clean' antimicrobial surfaces.

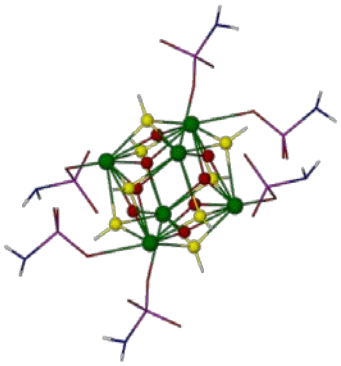
This project (which is done in collaboration with Prof. Michael Mehring at Universität Chemnitz) will investigate:

(i) the formation of novel bismuth(III) complexes which have high antimicrobial activity

(ii) reproducible methods for polynuclear bismuth oxido-cluster formation and

(iii) the incorporation of bismuth(III) and bismuth oxido-clusters into functionalized polymeric frameworks.

Antimicrobial testing against a wide range of gram positive and gram negative bacteria will be conducted on the mononuclear metal-organic compounds, on the corresponding oxido clusters, and finally on the organic-inorganic hybrid materials themselves.

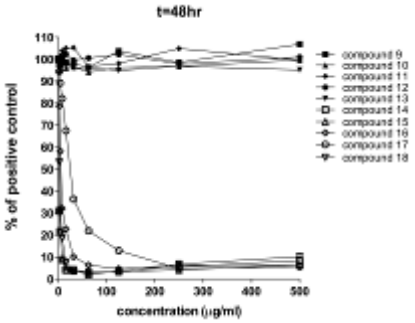


Bismuth oxido-cluster from sulfamic acid:
$[Bi_6O_4(OH)_4(SO_3NH_2)_6]\cdot H_2O$.

Development of New Bismuth-based Anti-Leishmania Drugs (with Dr Lukasz Kedzierski, *Walter and Eliza Hall Medical Research Institute)*

Leishmaniasis is a disease resulting from infection by the *Lieshmania* parasite and infects humans through contact with various animals, including sand-flys and dogs. It is estimated over 12 million people are currently infected and *ca.* 70,000 die annually. The two frontline drugs in the treatment of *Lieshmania* remain antimony (Sb) derivatives of gluconic acid; namely sodium stibogluconate (Pentosam©) and meglumine antimonate (Triostam©). These drugs are, however, highly toxic and are given as a series of painful intra-muscular injections over 28 days. It is necessary to develop new active drugs that are less toxic, cost effective, easy to synthesise and are orally active.

Bismuth sits below Sb in Group 15 and so they share many chemical features. However, Bi is considered to be the least toxic of all the heavy metals. The history of Bi compounds in medicine and the known anti-microbial activity of many Bi compounds we have the possibility of synthesizing new, active and safer *anti-Leishmanial* drugs. In recent years we have shown that bismuth carboxylates show high activity against the Leishmania parasite but that controlling toxicity toward mammalian cells is challenging. In the respect the ligand systems are important. This project will investigate the synthesis and characterisation of new bismuth complexes based on carbohydrate ligands and polyfunctional hydroxy sugar acids. These will be fully characterized, their synthetic reproducibility and purity established, and undergo *in vitro* testing against the *Leishmania* parasite. The student can, if they wish, learn how to grow the parasites in culture, how to infect macrophages and establish their efficacy against control systems.



The effect of substituted benzoic acids and their bismuth complexes on *L. major* promastigotes;

Prof. Stuart Batten

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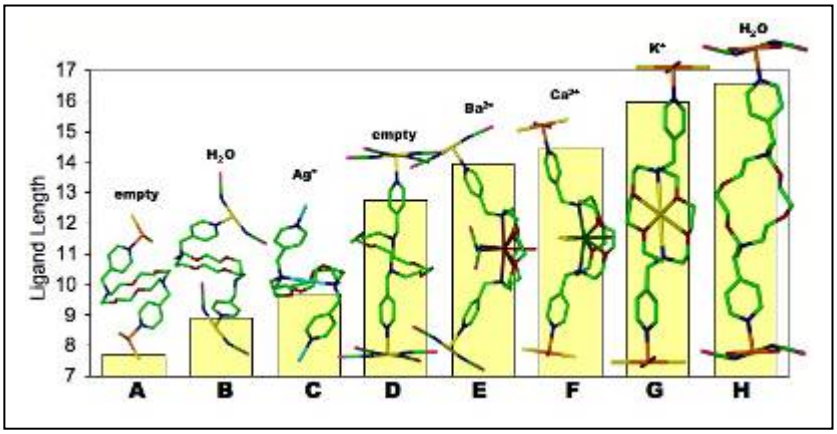
This document will give you an idea of the type of research we are undertaking within my group. All projects will involve aspects of organic and inorganic synthesis, and characterization by X-ray crystallography and other techniques. Students may do as little or as much crystallography as they wish (with the assistance of other group members), and we are regular uses of the Australian Synchrotron and the OPAL reactor at Lucas Heights. If you have any further queries, please do not hesitate to contact me.

For more information on my research, see: ***www.chem.monash.edu.au/staff/sbatten/index.html***

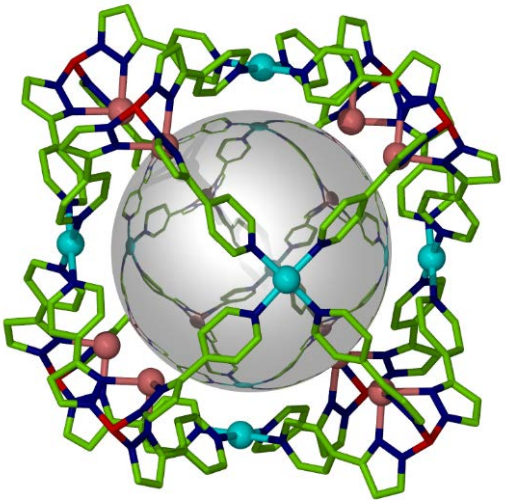
Coordination Polymers and Supramolecules of Variable Length Ligands

We have discovered a new type of bridging ligand, suitable for the construction of coordination polymers and supramolecules, in which the bridging length can be controlled by the presence or nature of e.g. group I or II metals (Duriska *et al.*, *Chem. Commun.*, 2009, 5579). The ligand contains a central crown ether cavity and peripheral metal binding pyridyl groups. In the absence of anything bound to the crown ether the bridging length is typically *ca.* 7.7 Å. In the presence of K^+, however, the bridging length more than doubles (*ca.* 16 Å). Other crown bound species (e.g. Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}) give intermediate bridging lengths. This new, completely unprecedented class of ligand opens up the way to new generations of materials such as sensors or porous materials in which the porosity can be varied (or even turned on and off) by e.g. the intercalation of different alkali or alkaline earth metals. This project will work towards this aim.



Multifunctional metallosupramolecules

Large (3 nm in diameter) spherical supramolecules (or 'nanoballs') have been synthesized in our laboratory (see Duriska *et al. Angew. Chem. Int. Ed.* 2009, **48**, 2549 & 8919; *ChemPlusChem* 2012, **77**, 616). Each molecule self-assembles from the reaction of six metal ions and eight copper complexes of a tris(pyrazolyl)borate derived ligand. These nanoballs can be made with a range of metal ions, and display some remarkable properties. These include the ability to switch between two magnetic spin states (spin crossover (SCO) between high spin and low spin). The SCO may be induced by change in temperature or, as a series of

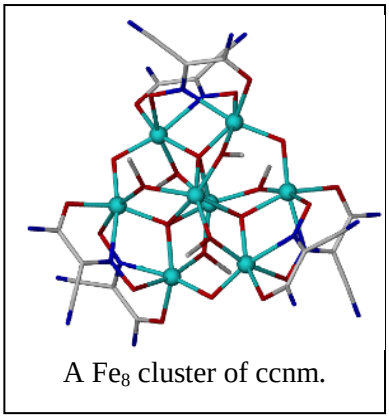


A 'Nanoball'.

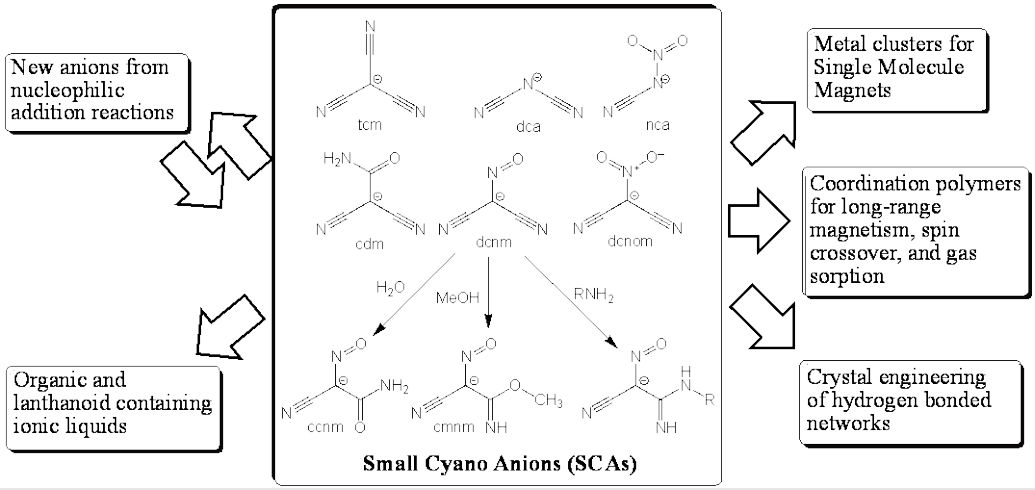
experiments in Bordeaux, France showed, irradiation of light. The molecular packing also creates cavities within the solid state, and thus the crystals will readily absorb solvents such as methanol, acetonitrile or acetone, and they have also been shown to absorb significant amounts of hydrogen, pointing to a new class of potential hydrogen storage materials, vital for the development of any future environmentally hydrogen based transport. They will also absorb CO_2, and thus have applications for carbon capture. Finally the nanoballs have also been shown to be effective catalysts for the conversion of 1,4-butanediol into THF. Thus these are truly multifunctional materials.
The aim of *this* project is to synthesise new nanoballs related to those described above. The project will involve the organic synthesis of new and known ligands, synthesis of new hollow coordination compounds of these ligands, and characterisation of their structures and properties (sorption of H_2, CO_2, CH_4, magnetic properties, catalytic properties).

Chemistry of Small Cyano Anions with Prof. Glen Deacon

We have been investigating the chemistry of small cyano anions, such as those shown below (*Chem. Commun.* 2011, **47**, 10189). They have shown some remarkable chemistry, including the synthesis of a large range of transition metal and/or lanthanoid clusters (up to and including a series of spherical Ln_{13} clusters ('Lanthaballs') – see Chesman *et al.*, *Chem. Eur. J.* 2009, **15**, 5203) which may have applications as single molecule magnets, interesting new coordination polymers and discrete complexes showing unusual packing motifs and ligand binding modes, new hydrogen bonding solid state networks, the nucleophilic addition of alcohols and amines (Chesman *et al.*, *Chem. Asian J.* 2009, **4**, 761) across the nitrile groups (e.g. cmnm is synthesized by addition of MeOH to dcnm), and the production of new ionic liquids. The versatility and range of applications of these anions is unprecedented, and has been extremely productive so far (30 papers from just two PhD students and a postdoc). This project will look at the synthesis of new polynitrile anions through nucleophilic addition and the investigation of their coordination chemistry with transition metal and lanthanoid metal ions, as well as the synthesis of new ionic liquids.



A Fe_8 cluster of ccnm.



Dr. Toby Bell

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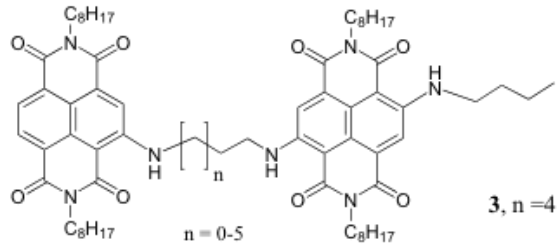
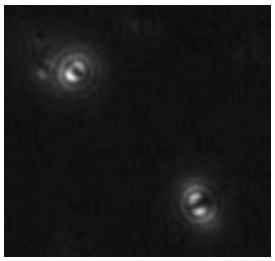
Probing energy transfer in single molecules (with Prof. Steven Langford)

It is now possible to study fluorescent materials at the ultimate limit of resolution: *one molecule at a time*. This approach reveals behaviour and phenomena obscured when studying a conventional bulk sample. New linked fluorophores based on substituted naphthalene diimide (SANDI) have been developed at Monash in the Langford group. Energy transfer from the mono-core-substituted half (left) to the di-substituted half (right) occurs with high efficiency. This project will examine the effect of the relative orientation between the two halves of the molecule on the rate of energy transfer in individual molecules. This will be done by visualising the emission patterns of single molecules and spectrally filtering the photons coming from each half of the molecule – the di-substituted moiety emits ~80 nm to the red of the mono-substituted. Orientation of the emitting portion of the molecule will be determined directly from the emission pattern and the efficiency of energy transfer from the relative intensity of the emission from the two halves.

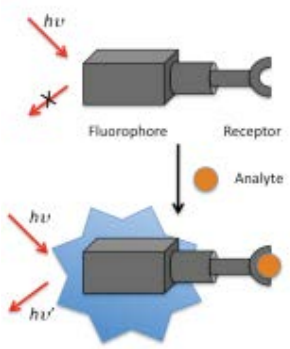




Structure of the linked SANDI energy transfer systems. (Left) Fluorescence emission patterns from single molecules. (Right) The shape of the pattern reveals the molecule's orientation

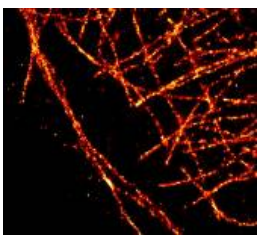
Fluorescence sensing at the single molecule level (with Prof. Steven Langford)

Fluorescence offers a versatile, highly sensitive and non-invasive means for sensing whereby a change in fluorescence output signals the occurrence of a binding event between the sensor compound and the target analyte. This project will take fluorescence sensing to the ultimate analytical level by detecting sensing events in single molecules. By doing this in a synchronised experiment for a small ensemble of single molecules, the distribution of reaction times for simple binding/unbinding reactions will be revealed for the first time. Sensors will include core substituted naphthalene diimides that can sense protons, amines, calcium and sodium cations, and fluoride anions.



Super-resolution microscopy of cell autophagy. (with Dr. Georg Ramm and Dr. Mark Prescott (School of Biochemistry))

Autophagy, literally "self eating", is a highly efficient recycling mechanism in cells and is the major degradation pathway for cellular organelles. Autophagy "cleans up" organelles such as damaged mitochondria, but can also rebuild nutrients during periods of starvation and is thus important for maintaining functional cells. Autophagy is emerging as a research theme in cancer biology and its regulation is crucial for understanding its role in cancer Autophagy is a highly compartmentalised pathway and understanding the spatial organisation of autophagic signalling

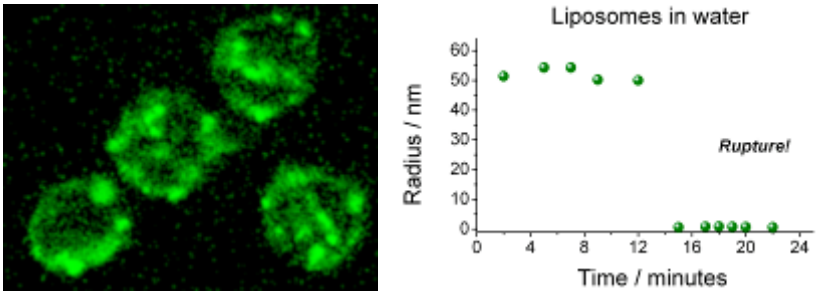


Super-resolution STORM image of microtubules in a HeLa cell. Spatial resolution is ~30-40 nm, an order of magnitude better than conventional fluorescence microscopes.

at a molecular level is therefore a critical step in determining mechanisms that could be targeted for therapeutic interventions. The origin of the autophagic structures is still debated many of the structures involved in autophagy are beyond the resolution limit of conventional fluorescence microscopy and to date have only been studied using electron microscopy (EM) which requires extensive sample perturbation including coating with a conductive metal such as gold. This project will use a newly developed "super-resolution" fluorescence spectroscopy technique (known as STORM) to image autophagic structures (~60-100 nm) directly in cells for the first time in order to unravel the cellular trafficking signalling network involved in autophagy. This will lead to new insights into how cells maintain correct function and ways to target unwanted cells such as cancer cells.

Armour piercing peptides for membrane rupture. (with Assoc.Prof. Lisa Martin).

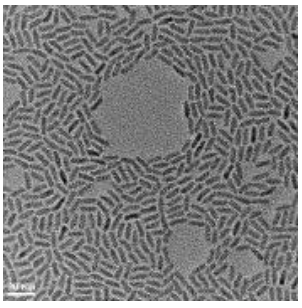
There is a subclass of peptides that are able to pierce the cell membrane producing a hole from which the cellular cytosol can leak out ultimately leading to cell death. This is being actively investigated as an alternative to antibiotics. Not much is known about the mechanism by which certain peptides are able to penetrate and rupture a membrane. This project aims to investigate this effect by capturing real-time fluorescence data of peptides penetrating membranes either as liposomes or coated on hollow polyelectrolyte capsules. A number of peptides will be investigated included the Tat peptide which is involved in translocation of HIV-1 virus into the cell interior. A key question is to determine the peptide to lipid ratio for effective rupturing to occur. Membrane specific effects involving bacterial and mammalian membranes will also be examined. The experimental techniques to be used are capable of measuring fluorescence from individual dye loaded liposomes.



Fluorescence image of dye loaded capsules (left) and diffusion data (right) showing sudden rupture of liposomes 20 minutes after addition of Tat peptide. Diameter of capsules is approximately 10 μm, while the liposomes are ~0.5 μm.

Defocused wide field imaging of CdSe nanodots and nanorods.(with Dr. Alison Funston)

Semiconductor nanocrystals such as CdSe quantum dots, nanorods and tetrapods are highly fluorescent and photostable. Their fluorescence wavelength may be modified by changing either the size or shape of the nanoparticle. These properties make them ideal as probes for single particle measurements and within imaging applications in biology. Nanorods and tetrapods have a much greater surface-to-volume ratio than spherical quantum dots and are therefore more prone to surface effects which reduce emission quantum yield. This project aims to take advantage of new precursor materials to synthesise nanorods and tetrapods with high quantum yields and well defined shape parameters.



Electron microscopy image of CdSe nanorods.

Unlike spheres, rods and pods have a well defined emission dipole. Production of bright samples will allow the direct measurement of emission dipoles of single particles by fluorescence microscopy for the first time. It will lead to knowledge about the nature of the emission dipoles and therefore the effect of these on energy transfer processes.

Professor Alan Chaffee

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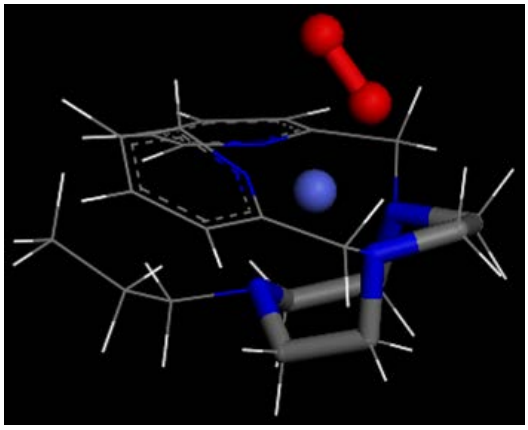
More information on our research can be seen at: ***www.chem.monash.edu.au/staff/Chaffee.html***

Supported Complexes for O_2 Separation from Air (with Dr Mohammad Chowdury)

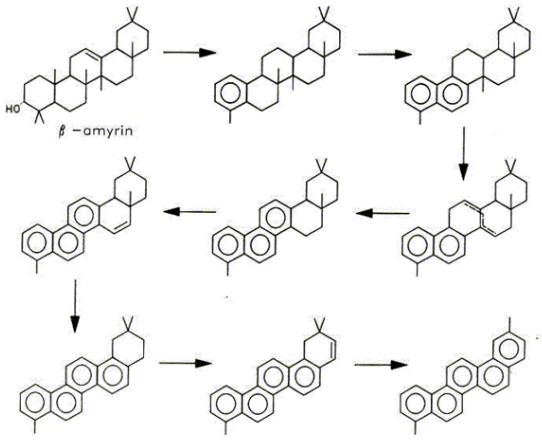
The search is on for better ways to capture, concentrate and sequester the CO_2 that is produced during electricity production. One way is to burn the coal with oxygen rather than air. This way the product (flue) gas consists only of CO_2 and H_2O. Water can be easily separated by condensation, leaving the CO_2 directly available for sequestration. Commercial O_2 separation, for example by cryogenic separation, is very energy intensive - so that there is need for a better approach. The project will focus on the development of adsorbent materials that can be used in a pressure swing adsorption process. The project will involve a mixture of computational chemistry, synthetic chemistry and physical evaluation focused on the development of Co-organo-metallic complexes dispersed on high surface area support materials. The combined results of computational and laboratory experiments will be used to identify and evaluate preferred ligands for selective O_2 separation.



Molecular model depicting molecular O_2 coordination with a Co(II) complex

Chemical Transformations of Fossil Organic Matter (with Dr Emma Qi)

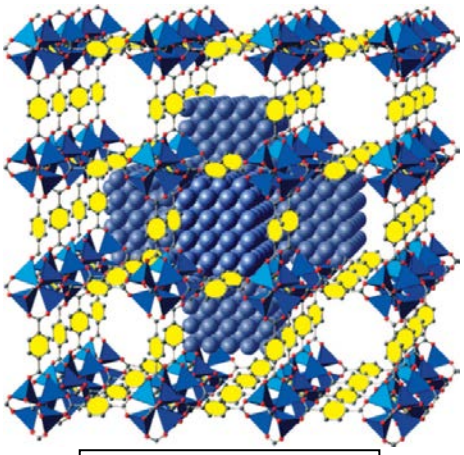
Organic matter deposited in sediments is subject to a range of chemical and microbiological processes. Under appropriate conditions the original organic matter may persist for many millions of years in a near pristine or partially altered state. In the lignite deposits of the Latrobe Valley macroscopic specimens of fossil wood, leaves, resins remain that are over 40 million years old, yet are morphologically distinct. Specimens will be collected, extracted with novel ionic liquids (eg, DIMCARB), and the extractable material will be evaluated by a variety of analytical techniques such as solid state NMR, GC-MS and pyrolysis-GC-MS. The objectives are (a) to delineate geochemical reaction mechanisms that occur in nature, such as that depicted in the figure and (b) to determine if the ionic liquids can selectively extract specific components that might be suitable replacements for petroleum derived chemical feedstocks.



Inferred geochemical transformations of naturally occurring β-amyrin into an aromatic hydrocarbon, dimethyl-picene.

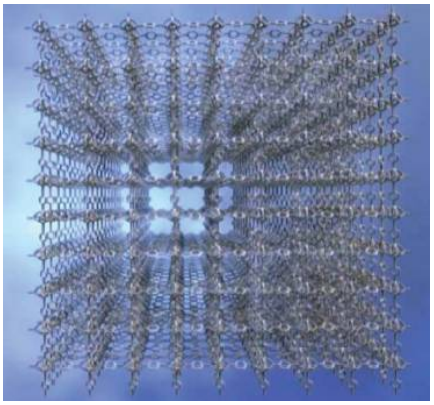
CO_2 Conversion to Higher Value Products (with Dr Anthony Auxilio)

This project seeks to convert CO_2, a waste product from electricity production, into useful products. The project will utilise a range of novel catlysts prepared from metal organic framework (MOF) structures onto which metals such as Cu and Zn will be immobilised. It is anticipated that these new materials will exhibit enhanced catalytic activity for the synthesis of methanol due to good metal dispersion combined with the inherent high surface areas of the MOFs themselves. Catalyst activity will be evaluated over a range of temperatures and pressures using new instrumentation (AutoChem 2950 HP). Product distributions will be determined by mass spectrometry (MS) and/or GC-MS.



MOF-5 with Cu incorporated

Inorganic-Organic Hybrid Materials for Greenhouse Gas Control (with Professor Stuart Batten and Brad Wells)



The project will involve a mixture of computational chemistry, synthetic chemistry and physical evaluation focused on the development of novel metal organic framework materials (MOFs) that can be used to separate and concentrate CO_2 from major emission points (such as the flue gas from power stations). Recent work has demonstrated that very high CO_2 adsorption capacities can be achieved with some of these materials. The results of computational and laboratory experiments will be compared to enhance our understanding of structure-property relationships. This will potentially allow CO_2 to be captured for reuse or long-term storage (sequestration).

Causes of Spontaneous Combustion of Victorian Brown Coal (with Dr Emily Perkins)

Victoria has large reserves of easily accessible brown coal, but this cannot be exported due to the propensity to undergo spontaneous combustion. This project looks at the factors (both chemical and physical) that affect the propensity of brown coal to spontaneously combust. It will examine the low temperature oxidation behaviour of brown coal and dried brown coal products. A comparative study of brown coal products with different chemical and physical properties is planned using a variety of techniques – including thermogravimetric analysis (TGA) and the "wire basket" method. O_2 adsorption on various coal surfaces will be quantified, as will porosity and the concentration of trace inorganic components.

Dr. Perran Cook

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This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me (details above).

More information on my research can be seen at: ***www.chem.monash.edu.au/staff/cook.html***

Nitrification kinetics in permeable sediments

Nitrogen is the nutrient that generally limits algal growth in marine waters. Humans have doubled the rates at which bioavailable nitrogen enters the biosphere through the Haber Bosch process, causing eutrophication (algal blooms) as well as greatly altering the nitrogen cycle. The nitrification reaction is a critical part of the nitrogen cycle and can be summarized as follows

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

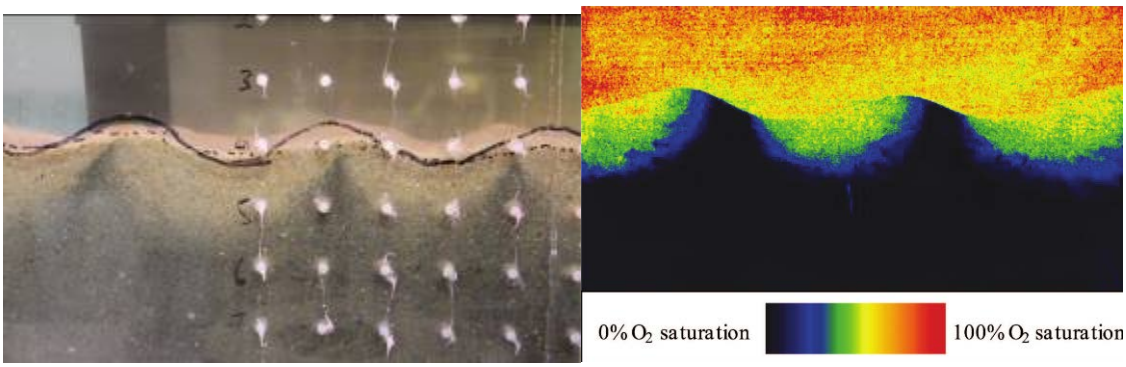
The reaction is mediated by the bacteria nitrosomonas and nitrobacter, which are chemoautotropic and derive their energy from this reaction. The reaction is an essential link in the nitrogen cycle because it produces NO_3^-, which is an essential precursor to the denitrification reaction, which leads to a net loss bioavailable nitrogen in the biosphere. Nitrification and denitrification are often closely coupled in sediments. Permeable sediments (sands) form the majority of continental shelf sediments, yet there have been no studies on the kinetics of this reaction in this type of environment. This project will quantify the kinetics of denitrification in different sand types within Port Phillip Bay using flow through reactors (pictured).

How does flow affect denitrification in permeable sediments?

Porewater flow through sandy sediments leads to distinct patterns of solute and geochemical reactions within the sediment (see below). Denitrification is a geochemical reaction of particular importance because it is a sink for bioavailable nitrogen, converting NO_3^- to N_2 gas under anaerobic conditions.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2\ (g)$$

This project will explore how changing current speed affect rates of denitrification within permeable sediments using a combination of a flume, planar optodes to measure O_2 concentration and stable isotopes to quantify denitrification.

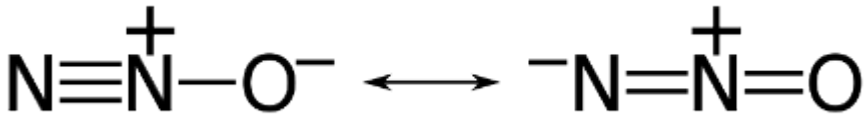


Figures illustrating how water flow through sand ripples affects iron monosulfide distribution (left) and oxygen distribution (right) within the sediment measured using a planar optode.

Stable isotopes as a tool to identify sources of N_2O

Co supervisor: Assoc Prof. Mike Grace

N_2O is a potent greenhouse gas, which has a global warming potential 310 times that of CO_2, and the concentrations in the atmosphere are rising. N_2O is naturally produced as a byproduct from two key nitrogen cycling processes nitrification and denitrification. Identifying the relative importance of these reactions is complicated. Nitrogen exists as two naturally occurring isotopes, ^{14}N (99.63%) and ^{15}N (0.37%), and the ratios of the two isotopes on the inner and outer nitrogen (see structure below) can help identify the production pathway of nitrous oxide. This project will set up a method to quantify the site preference of N_2O using an isotope ratio mass spectrometer and apply the method to identify sources of N_2O in locations around Melbourne that are known to be significant sources of N_2O (wetlands and groundwater)

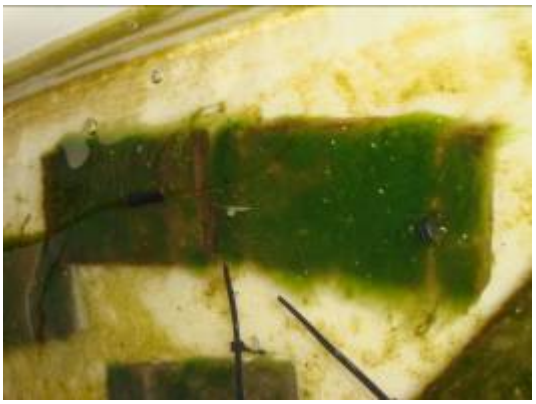


Are epiphytic algae a net source or sink of nitrogen in wetlands?

Co supervisor: Assoc Prof. Mike Grace, Prof John Beardall (Biology)

This project is best suited to a mid-year intake

Eutrophication is caused by excess nitrogen and phosphorus entering our waterways and is a major threat to aquatic ecosystems, causing excess algal growth which ultimately leads to a loss of amenity and ecological integrity. Denitrification is a crucial nitrogen cycling pathway because it removes bioavailable nitrogen from aquatic ecosystems and is thus an ecologically important process because it can remove excess nitrogen from anthropogenic sources. Denitrification is an obligately anaerobic process and to date, most studies of denitrification have focused on the sediment. Recent measurements have shown that algal growths colonizing hard substrates also have high denitrification rates. Paradoxically, epiphytic algae may also be significant source of nitrogen through the process of N_2 fixation if cyanobacteria are present. This project will investigate the relative important of these two processes in a selection of water treatment wetlands around Melbourne.



Professor Glen Deacon

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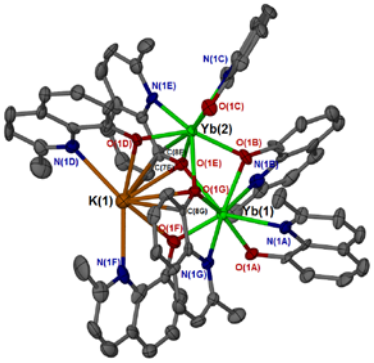
For more information, see: www.chem.monash.edu.au/staff/deacon.html

Rare earth elements

Rare earths are currently seen as the strategic materials of the 21st century. with considerable international concern over the Chinese domination of the supply of separated elements and compounds. Our group provides the fundamental knowledge base to underpin industrial developments in the area. Rare earth elements comprise Group 3 (scandium, yttrium, lanthanum) and the lanthanoid elements (cerium-lutetium). Australia has abundant rare earth resources which have been mainly neglected despite their widespread uses, e.g. ceramic supports for exhaust emission catalysts, alloy magnets in all car engines, catalysts for artificial rubber production, and magnetic imaging. Potential applications include green corrosion inhibitors (below). Their metal-organic chemistry is a major new frontier and is generating great excitement, for example in the discovery of new oxidation states. We are particularly interested in high reactivity rare earth organometallics (Ln-C), organoamides (Ln-NR_2) and aryloxides (Ln-OAr), and have developed unique synthetic methods to obtain them. Features of these compounds include unusual stereochemistry, low coordination numbers and extraordinary reactivity. To prepare and structurally characterize the compounds represents a major challenge. **The program involves extensive international collaboration.** The relatively low toxicities of these elements, also makes them attractive for industrial (GREEN) processes.

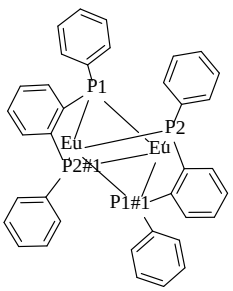
Heterobimetallic complexes (with Prof. Peter Junk (JCU) and Dr David Turner)

Controlled syntheses of bimetallic complexes pose a major challenge with the products of great interest as they combine features of both metals. Thus catalytic, magnetic, luminescence properties potentially have new features. Projects involve combinations of rare earth elements (Ln) with alkali or alkaline earth metals (Ae) or transition metals (M). Both high reactivity systems (with alkoxide/aryloxide/pyrazolate ligands) and air-stable systems (with oxinate, carboxylate and chelation stabilized ligands) are being investigated. Syntheses include direct reactions of metals and elevated temperature solid state rearrangements. The studies represent a bridge between metal-organic and solid state chemistry, and as such they represent a major new initiative in inorganic synthesis. Besides X-ray crystallography and powder photography, use of vacuum/N_2 lines and dry box technology is a feature. Access to the Australian Synchrotron enables examination of very small crystals.

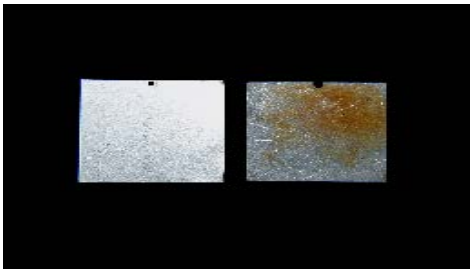


Phosphidolanthanoid complexes – a bridge to unusual oxidations states (with Dr A. Stasch and Prof. Peter Junk (JCU))

Isolation of lanthanoid complexes in unusual oxidation states, e.g. Y^{II} has been a frontier science development in recent years, and the first Nd^{II} organometallic was prepared at Monash (Angew. Chem. Int. Ed. 2009, **48**, 1117). The diphosphido complex shown in the Figure has been isolated as a 1,2-dimethoxyethane complex in a fortuitous synthesis. Development of a reliable synthesis to this compound and analogous Yb^{II} and Sm^{II} complexes is a major challenge. If it can be achieved the Ln^{II} complexes have great potential for interesting redox chemistry.



Green Corrosion Inhibitors (with Prof. Peter Junk (JCU), Dr David Turner and Prof. Maria Forsyth (Deakin University))



The cost in Australia alone due to corrosion of steel piping in recirculated water systems amounts to millions of dollars per year. To date, the most widely used inhibitors to combat corrosion in these systems have been based on chromates and nitrates. These are now recognised as being harmful to health and the environment, and their use is being discouraged and alternatives sought. This project involves the development of novel compounds based on the benign rare earth elements, coupled with an organic corrosion inhibitor (such as a carboxylate anion), to provide bifunctional corrosion inhibitors with synergistic properties. Modelling the corrosion inhibition involving preparation of heterobimetallics between lanthanoids and aluminium is proposed. The Figure shows visible signs of corrosion protection on a steel coupon after 7 day immersion (left) and unprotected (right) in 0.1M NaCl with and without 500 ppm [Ce(salicylate)$_3$.H$_2$O] respectively.

New Approaches to Metal-Based Syntheses (with Prof. Peter Junk (JCU))

A distinctive feature of our synthetic approach to rare earth organometallics, organoamides, and organooxides has been the use of reactions starting with the rare earth metal or even one of the alloy magnets used in electric motors. As these have mainly used organomercurials or organothalliun reagents we are exploring greener alternatives. Three approaches have potential to succeed. (a) use of iodine to activate the rare earth metal, (b) use of the much less toxic triphenylbismuth, (c) use of lanthanoid pseudo-Grignard reagents such as PhYbI, MeEuI etc. Examples of each of these exciting possibilities follow:

(a) $Ln(I2) + 3LH \rightarrow LnL_3 + 3/2H_2$

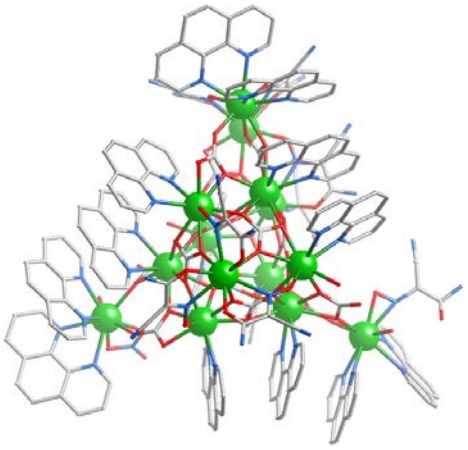
(b) $2Ln + 3BiPh_3 + 6\,LH \rightarrow 2LnL_3 + 3Bi + 6PhH$

(c) $PhLnI + LH \rightarrow LLnI + PhH$ LH can be a pyrazole, phenol, amine, amidine etc (see Chem. Commun. 2010, 46, 5076)

The product from (c) can be further elaborated by oxidation or metathesis reactions.

New Materials Derived from Small Cyano Anions (with Prof. Stuart Batten)

Small cyano anions such as dicyanonitrosomethanide, $[C(CN)_2NO]^-$ (dcnm) and their alcohol, water and amine addition products are novel, potentially divergent ligands with the capacity to bind both transition metals and lanthanoid elements or both to give polymers and cages of interest as new materials with novel magnetic properties. They have already enabled the synthesis of new 12 coordinate lanthanoid complexes $[Ln(\eta^2\text{-dcnm})_6]^{3-}$ and carbanatolanthaballs as illustrated by the beautiful Gd_{14} Gadoball.



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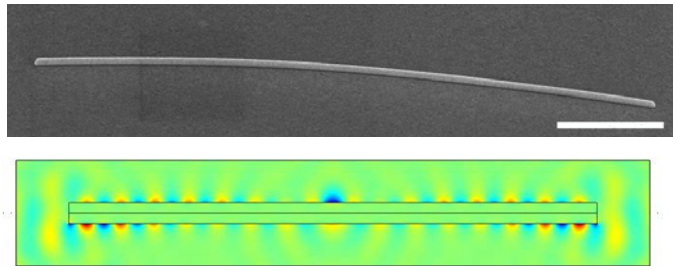
If you have any further queries, please do not hesitate to contact me (details above). More information on my research can be seen at: ***www.chem.monash.edu.au/staff/funston***

Synthesis of Nanoscale Optical Fibres from Nanoparticles

The largest challenge facing the electronics industry is the further miniaturisation of electronic circuitry. One promising approach is the use of optical circuitry, which has potential to increase the speed of current electronic circuitry whilst also leading to its further miniaturisation. In order to achieve this, the light must be guided and confined to the nanoscale. Gold and silver nanowires are known to act as nanoscale optical fibres, transmitting light and guiding it from one end of a nanowire to the other. Linear arrays of gold and silver nanoparticles are also able to guide light at the nanoscale and have potential to do this more efficiently than a single nanowire. This project involves the synthesis of linear arrays of gold and silver nanoparticles for waveguiding applications and the testing of the ability of the arrays to transmit light. This project involves the chemical synthesis of nanomaterials, their characterization using scanning electron microscopy (SEM) and dark-field microscopy, and determination of the efficiency of waveguiding of the linear arrays. A number of projects are available in this area.

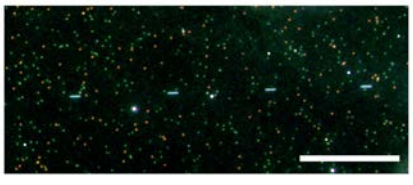
Ag nanowire



Transfer of light through an Au nanowire

Synthesis of Coloured Assemblies of Nanoparticles

Gold nanocrystals are highly coloured due to their localised surface plasmon resonance. When two nanoparticles are close to one another, their localized surface plasmon resonances interact and their colour changes. The colour of the coupled resonance is dependent upon the distance between the particles and this effect was recently used to measure the distance between two biological molecules in solution. This project involves the assembly of a number of nanoparticles to create nanoparticle superstructures of well-defined geometries. These will include nanoparticle dimers, trimers and heptamers (flowers). The nanoparticles will be assembled using organic linkers. The aims of this project are to 1) investigate the conditions under which the nanocrystal:linker system is colloidally stable 2) assemble a number of nanoparticles into pre-defined geometries and improve the yield of the assembly, 3) modulate the linker properties, and therefore the assembly geometry and separation between particles and 4) investigate the scattering spectrum (colour) of the assemblies and their response to polarized light. The resulting assemblies will have unique optical properties with applications in sensing, metamaterials smart optical films as well as adding to our understanding of nanoparticle coupling. The project will include the synthesis of metal nanoparticles, their assembly, the use of dark-field microscopy to measure the Plasmon resonance of the assembly and scanning electron microscopy (SEM) for the characterization of the assemblies.



(Right: Dark-field image of single Au particles)

Nanocrystal Sensors: Real-time Drug Transportation into Cells

(with Assoc. Prof. Lisa Martin and Prof Don McNaughton)

In biological systems the cell membrane mediates the entry and exit of molecules into (or out of) the cell. The cell membrane thus mediates signaling processes; in addition, many proteins are bound within membranes. The membrane of a red blood cell (without its cellular components) is known as a ghost cell and the potential exists for these to be used as a vehicle for drug delivery, with the drug encapsulated within the cell for transport. To achieve this, the entry and exit of molecules, proteins and peptides across the cell membrane must be understood. This project aims to use the change in a gold nanoparticles' plasmon resonance to sense biological molecules within, and their transport through a cellular bilayer. These include (i) the binding of a ligand to a membrane-bound protein receptor, (ii) Transmembrane 'carrier' peptides and (iii) molecular transport across the cell membrane. This will involve the synthesis of gold nanoparticles and their characterization via microscopy (TEM, SEM, AFM) and optical spectroscopy (UV-visible spectroscopy and dark-field microscopy). Initially, ghost cell membranes will form a membrane bilayer, incorporating a receptor, over gold nanorods and changes in the plasmon resonance as a result of receptor binding will be tracked.

How does the Atomic Level Nanoparticle Shape Effect the Nanoparticle Colour?

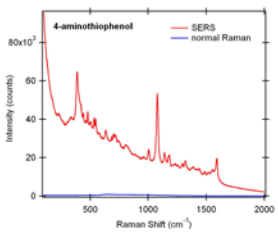
(with Assoc. Prof. Joanne Etheridge (MCEM), Prof Paul Mulvaney (University of Melbourne))

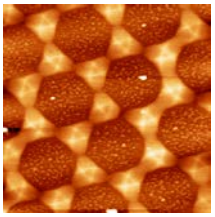
This is a fundamental question that underpins the development of metal nanoparticles for applications in optoelectronics, nanophotonics, sensing and biomedical sciences. However, our understanding of nanoparticle colour is limited by our understanding of the boundary conditions (in this case, nanoparticle shape) that define them. Small changes in the 3D structure of a metal particle, such as a change in the geometry of a nanorod endcap and surface roughness have a significant effect on the energy of the plasmon resonance. This project aims to correlate the 3D atomic structure of individual gold nanoparticles with their respective optical resonances. This will involve the synthesis of gold nanoparticles, measurement of single nanoparticles' plasmon resonance via dark field microscopy using a correlation technique to allow identification and investigation of the same particle using TEM.

Nanofabrication of Substrates for Surface-Enhanced Raman Spectroscopy

(with Prof Don McNaughton and Dr Fiona Scholes (CSIRO))

Surface-enhanced Raman spectroscopy (SERS) has become an area of intense interest in recent years, spurred by a growing desire to detect analytes (in areas such as water safety and bioterrorism prevention) with ever-increasing speed and sensitivity. It is a highly versatile analytical method, providing spectroscopic fingerprints of chemical and biological materials with significant signal enhancements over normal Raman scattering. The aim of this project is to utilise state-of-the-art nanofabrication tools, to engineer surfaces for SERS and to harness these surfaces for controlled aggregation of SERS-active Au nanoparticles.




AFM image of Au triangles

Assoc. Prof. Mike Grace

Room no. G25c (Water Studies Centre), Tel: 9905 4078, email: mike.grace@monash.edu

The focus of many of these projects can be modified to suit the interests of the student – from physical, analytical and/or environmental chemistry and biogeochemistry through to aquatic and/or restoration ecology. Two projects are available for students who wish to combine synthetic and environmental chemistry.

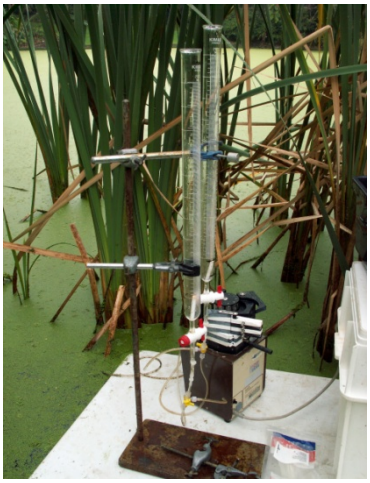
Assessing the impacts of pharmaceuticals on aquatic ecosystems (with Prof Philip Marriott)

Awareness of the effects of common pharmaceuticals on organisms (insects, fish) living in streams and lakes has slowly emerged over the last decade. Apart from one recent conference poster which showed dramatic reductions, there has been no published study on how these pharmaceuticals can affect rates of fundamental ecosystem processes. This project will use novel pharmaceutical diffusing substrates to investigate effects of common drugs like caffeine, an antibiotic and an antihistamine on photosynthesis, respiration and biomass formation in urban waterways. As well as investigating the potential major impacts of these chemicals on the health of aquatic ecosystems, the student will utilise state-of-the-art chromatographic separation and identification equipment within the School of Chemistry.

Constructed wetlands – environmental benefactors or villains?

This project will examine the extent to which wetlands around Melbourne generate greenhouse gases (GHGs) including CH_4, N_2O and CO_2. The prevailing wisdom is that wetlands must be beneficial for the environment as they are designed to remove nutrients and other pollutants from stormwater in urban creeks. However, previous work in the Water Studies Centre has shown that under a range of relatively common conditions, wetlands can also generate significant quantities of GHGs. This project will measure rates of GHG production in several wetlands around Melbourne and develop understanding of the key wetland characteristics and conditions that control production. Experimental work will involve field measurements and laboratory mesocosm (sediment core) investigations.

How does vegetation enhance nitrogen removal in waterways? (with Dr Perran Cook)

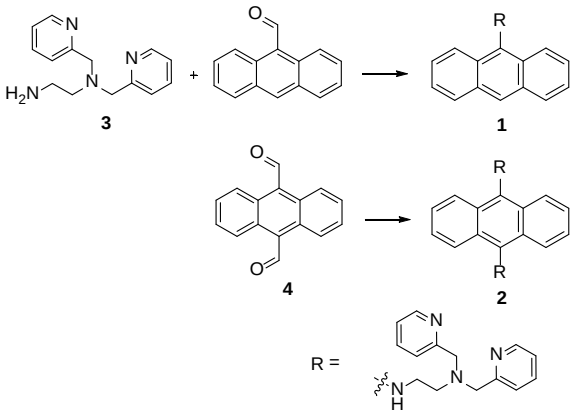


Many of Melbourne's wetlands have been constructed with the primary aim of removing nitrogen from stormwater. A variety of vegetation is planted to assist with nutrient removal. However, the effectiveness of different types of vegetation for N removal is poorly understood and documented. This project will involve addition of isotopically-enriched $^{15}NO_3^-$ (stable, not radioactive!) to the root zones of several common wetland plants to follow the fate of the nitrate. Ideally the nitrate will be denitrified to N_2 gas but may also be converted to the potent greenhouse gas, N_2O, or reduced to $^{15}NH_4^+$. The project will make use of the new isotope ratio mass spectrometer in the Water Studies Centre and will involve both field work in Melbourne wetlands and laboratory-based studies. This work will inform effective management of Melbourne's waterways as well as enhancing understanding of the role of plants in sediment biogeochemistry.

Developing an Ion-Exchange Medium with High Nitrate Affinity (with Prof Steve Langford)

Nitrate pollution is one of the greatest threats to many coastal waterways, including Port Phillip Bay. Excess nitrate can initiate major algal blooms with devastating effects. New isotope-based techniques can identify the origins of the nitrate e.g. does it come from industrial effluent, or agricultural practices? These isotope techniques require concentrated nitrate solutions, which are not often found in the natural environment, hence difficult and expensive preconcentration methods are required, to obtain sufficient nitrate without also getting high concentrations of chloride. Our joint research groups have been working towards a solution. We have recently prepared resins that show promise in nitrate selectivity and hence an ion-exchange-like material. The resins formed in this project will be derivatives of our lead and will be tested for nitrate exchange capacity, specificity for nitrate over other common anions (especially chloride) and then used for preconcentrating nitrate from a range of natural water samples for subsequent isotopic analysis. *This project is ideally suited to a student with interests in both synthetic and environmental chemistry.*

Developing a chemosensor for measuring heavy metals at environmentally important concentrations. (with Dr Kellie Tuck)



Heavy metals including Zn, Cd and Pb, in cationic form, may cause severe environmental problems in our waterways, but measurement of cation concentrations rather than the total concentration is very difficult and tedious. Recent work in Dr Tuck's lab (Tetrahedron Letters 51 (2010) 1161–1165) has described a novel, fluorescence based chemosensor to detect environmentally relevant concentrations of Zn^{2+}. This breakthrough allows easy determination of the free cation as it is only this form which is associated with toxicity. This project will expand the capabilities of this class of molecular probes by synthesis of existing and new target fluorescent moieties and then use these new probes to assess the threat posed to several Melbourne wetlands by heavy metal pollution. *This project is ideally suited to a student with interests in both synthetic and environmental chemistry.*

Professor Milton T. W. Hearn

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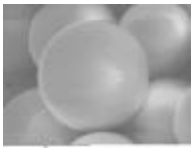
More information on our research can be seen at: ***http://www.chem.monash.edu.au/green-chem/***

Analysis of polar compounds by green aqueous chromatography

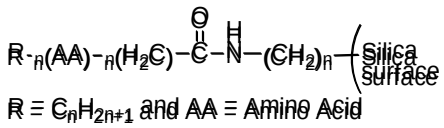


Assoc. Supervisors: Dr Reinhard Boysen, Dr William Yang

In the framework of analytical green chemistry, this project explores the use of aqueous normal-phase chromatography (ANPC) as an alternative to traditional reverse-phase chromatography for the separation of polar compounds with minimised environmental footprint. The aim is to develop the design rules of micro-analytical ANPC methods for the analysis of various polar compounds, including natural products, nutraceuticals and pharmaceuticals.

Development of functional monolithic silica capillary columns for CEC

Assoc. Supervisors: Dr Jamil Chowdhury, Dr William Yang, Dr Reinhard Boysen



Monolithic stationary phases have found applications in microanalytical separation systems, *e.g.*, capillary electrochromatography (CEC), micro-HPLC and chip technologies. In this project, new silica-based monolithic capillary columns with varying degrees of porosity will be prepared and functionalized with amino acid and alkyl-based ligands with different polarity/hydrophobicity and helicity. These new columns will then be assessed for their performance as stationary phases in CEC.

Synthesis of metal chelating polymers for water treatment applications

Assoc. Supervisors: Dr Simon Harris, Dr Shahid Kazi

The heavy metals lead, mercury and cadmium, and the metalloid arsenic are highly toxic to humans, animals and marine organisms. Contamination of water supplies with these toxic metals may occur from industrial or natural sources. This project aims to design and synthesise novel metal-chelating polymers for water-treatment applications.

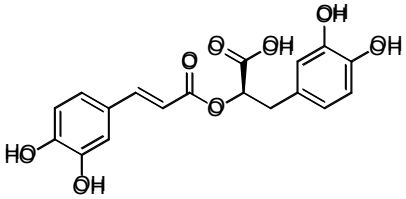
Characterisation of PEGylated proteins and peptides

Assoc. Supervisor: Dr Simon Harris

PEGylation, the covalent attachment of polyethylene glycol (PEG) polymers to compounds, has become one of the best validated drug delivery methods for therapeutic proteins. This project aims to investigate and optimise structural aspects of protein PEGylation using mass spectrometry-based peptide mapping.

Synthesis and characterisation of rosmarinic acid derivatives as inhibitors of platelet aggregation

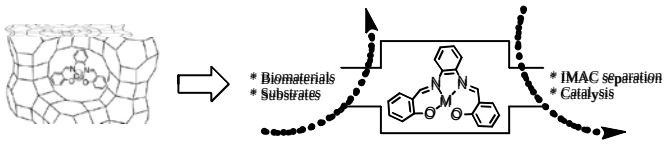
Assoc. Supervisors: Dr Simon Harris, Mr Basil Danylec



The identification and synthesis of new inhibitors of platelet aggregation as treatments for heart attack and stroke patients is a very active area of research and development. Rosmarinic acid, a natural product found in common plants and herbs, is an inhibitor of platelet aggregation. This project will involve the synthesis of a small library of rosmarinic acid derivatives that will be evaluated for their effects as inhibitors of human platelet aggregation. These compounds will also be used as templates for the preparation of molecular-imprinted polymers (MIPs) for the extraction of rosmarinic acid and other valuable bioactives from sustainable renewable resources.

Zeolite-based metal complex systems for bioseparation and biomimetic catalysis

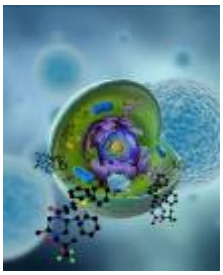
Assoc. Supervisor: Dr Shahid Kazi



This project involves the development of zeolite-based 'ship-in-a-bottle' metal complexes where the complex will be synthesised in the super cage of the zeolite and therefore locked into the pocket. These locked complexes will then be evaluated for application in bioseparations and biomimetic catalysis.

Synthesis of more effective anti-cancer drugs

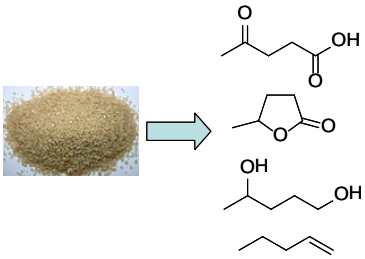
Assoc. Supervisor: Dr Geoff Kelso, Mr Basil Danylec



Many different anti-cancer drugs used in the clinic today are plagued by eventual drug resistance and debilitating side-effects. This project aims to overcome these problems by synthesizing new types of anti-cancer drugs based on novel compounds that selectively accumulate in cancer cells and disrupt abnormal metabolic pathways essential to their survival. Newly synthesized drug candidates will be assessed in cell-based assays to determine their potential for further development.

Catalytic conversion of sugars to industrial platform chemicals

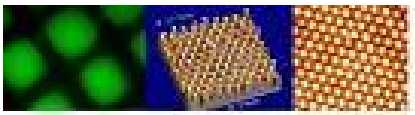
Assoc. Supervisors: Dr Mahesh Potdar, Dr Geoff Kelso



The sugar molecules sucrose, glucose and fructose are produced from renewable biomass and are potential sustainable resources for the chemical industry to draw upon to produce essential chemicals, fuel additives and polymeric materials currently produced from unsustainable fossil fuel resources. In this project, new types of catalysts will be developed for converting these sugars to valuable platform chemicals.

Synthesis and characterisation of molecularly-imprinted polymer films

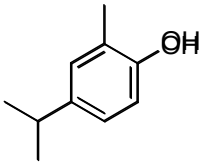
Assoc. Supervisors: Dr Lachlan Schwarz, Dr Jamil Chowdhury, Dr Reinhard Boysen



The aim of this project is to design, synthesise and characterise molecularly-imprinted polymer (MIP) films suitable for biosensor applications in medicine and analytical chemistry. This will entail the development of appropriate polymerisation chemistries aided by molecular modeling and NMR-spectroscopy, the synthesis of thin MIP films via spin-coating procedures and the application of advanced spectroscopic characterisation methods.

Development of a molecular imprinted polymer to extract bioactive compounds from sustainable natural resources

Assoc. Supervisors: Dr Lachlan Schwarz, Dr Sab Ventura, Mr Basil Danylec



Carvacrol is a naturally occurring terpene with a number of beneficial pharmacological actions. We aim to use this molecule as a template to generate a novel polymer to continue our studies into molecularly imprinted polymers (MIPs). Analytical studies will explore this polymer's ability to bind compounds with similar structural motifs, and lead to a protocol for the extraction of carvacrol and structurally similar compounds from plant sources. Extracts obtained will also be evaluated using human cancer cell lines.

Professor Cameron Jones

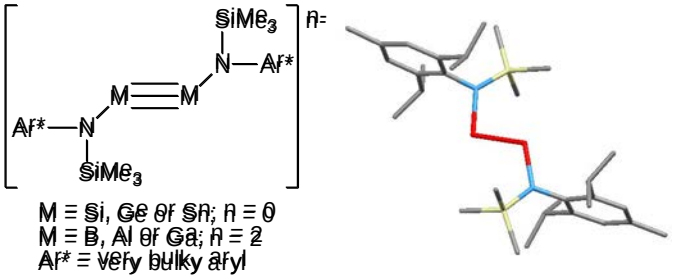
Room No. 110, Tel: 9902 0391, email: cameron.jones@monash.edu

Modern Main Group Chemistry

In the past 5 years remarkable progress has been made in the chemistry of very low oxidation state and low coordination number s- and p-block compounds. It is now possible to prepare and investigate the fascinating reactivity of compounds that were thought incapable of existence until a few years ago. This area is rapidly expanding in the US and Europe but is under-studied in Australia. The following Honours projects are currently available:

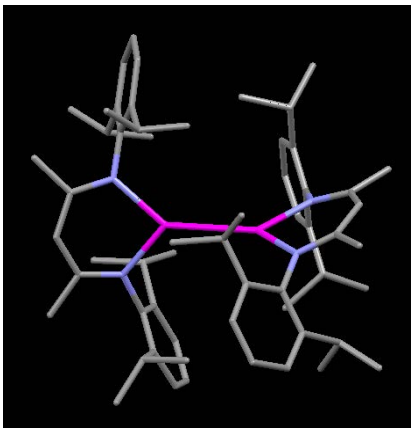
Main group metal-metal multiply bonded systems: replacements for transition metal catalysts?

In recent years "trans-bent" compounds containing multiple bonds between two p-block metal(I) centres have been stabilised by ligation with extremely bulky alkyl or aryl substituents (R). These include the remarkable heavier group 14 analogues of alkynes, *viz.* RE≡ER (E = Si, Ge, Sn or Pb). In this project you will prepare the first examples of related bulky amido substituted "metalynes" (see picture) and explore their use for the reversible reductive activation of H_2, CO_2, NH_3, ethylene etc. If this can be achieved, the exciting possibility exists to use such compounds as replacements for expensive and toxic transition metal catalysts in numerous industrial processes; and for the conversion of the Greenhouse gas, CO_2, to useful chemical products.



see: (i) *Angew. Chem. Int. Ed.*, 2012, **51**, 8611; (ii) *J. Am. Chem. Soc.*, 2012, **134**, 6500; (iii) *J. Am. Chem. Soc.*, 2011, **133**, 10074; (iv) *Nature*, 2010, **463**, 171.

Stabilisation and application of complexes of Group 2 metals in the +1 oxidation state. (with Dr. A. Stasch)

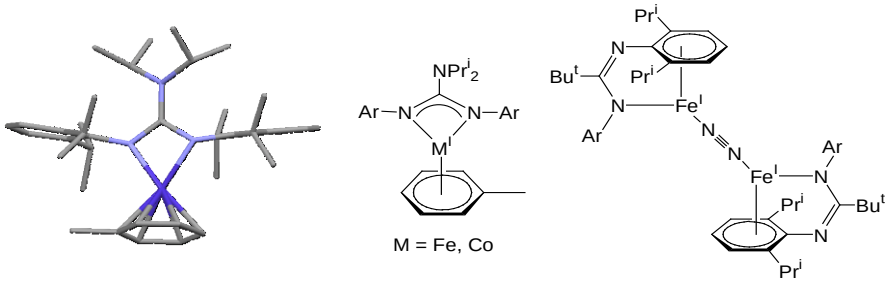


It has previously been only possible to prepare compounds containing the Group 2 metals (Be, Mg or Ca) with the metal in the +2 oxidation state. Recently, we have reversed this situation with the landmark preparation of the first thermally stable compounds to contain Mg-Mg bonds (e.g. see picture). The formal oxidation state of the magnesium centres in these compounds is, therefore, +1. As a result, these species are highly reducing, a situation which has lent them to use, in our laboratory, as specialist reagents in organic and organometallic synthetic methodologies. You will further explore this potential, in addition to examining the possibility of preparing the first dimeric calcium(I) compounds. Furthermore, you will examine the use of such systems as soluble models to study the reversible addition of dihydrogen to magnesium metal (yielding MgH_2). This poorly understood process is of great importance for future hydrogen storage technologies which will be essential for viable zero emission vehicles powered by fuel cells.

see (i) *Science*, 2007, **318**, 1754; (ii) *Angew. Chem. Int. Ed.* 2009, **48**, 9701; (iii) *J. Am. Chem. Soc.* 2009, **131**, 4208; (iv) *Nature Chem.*, 2010, **2**, 865; (v) *Chem. Eur. J.,* 2012*,* **18***,* 10669.

Stabilisation and application of novel low oxidation state d- and p-block metal heterocycles

Through our work on the stabilisation of novel gallium(I) heterocycles we have found that the bulky amidinate and guanidinate ligands developed to access these compounds can be applied to the preparation of previously inaccessible heterocycles containing low oxidation state metal centres from across the periodic table (e.g. see picture). We have subsequently discovered that these highly reactive compounds have enormous potential to be applied to, for example, small molecule activation, catalysis and enzyme mimicry. You will extend this work and investigate the preparation of new transition metal(I) and p-block element(I) heterocycles and their application to the activation of N_2, CO_2, H_2 etc. One eventual aim of this study is the catalytic conversion of dinitrogen to ammonia at room temperature, which remains one of the holy grails of chemistry.



see (i) *Angew. Chem. Int. Ed.*, 2012, **51**, 8294; (ii) *Chem. Commun.*, 2012, **48**, 2504; (ii) *J. Am. Chem. Soc.*, 2011, **133**, 10074; (iii) *Angew. Chem. Int. Ed.*, 2009, **48**, 7406; (iii) *Chem. Eur. J.* 2010, **17**, 1294.

N.B. In all of these projects you will learn the very latest techniques for the synthesis, manipulation and characterisation of very air sensitive compounds.

Professor Steve Langford

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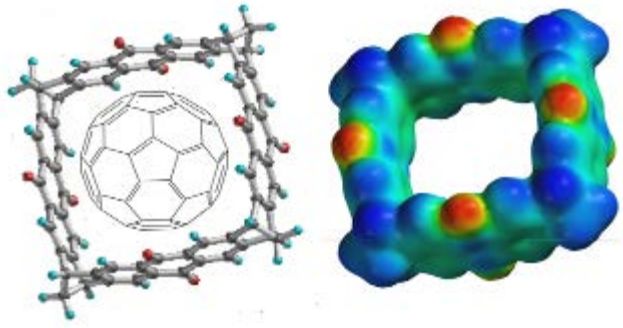
More information on our research can be seen at:
www.chem.monash.edu.au/staff/langford.indexhtml

Supramolecular chemistry offers a paradigm shift for fundamental chemical research leading from a bio-inspired discipline to one with a focus on the development of emerging technologies in the sciences and related disciplines. My group's research focuses on organic-based supramolecular systems for use in materials science and in diagnostic applications. We combine the elegance of organic synthesis with the need for physical and analytical characterization of the molecular assemblies we form. These techniques include electrochemistry and fluorescence spectroscopy.

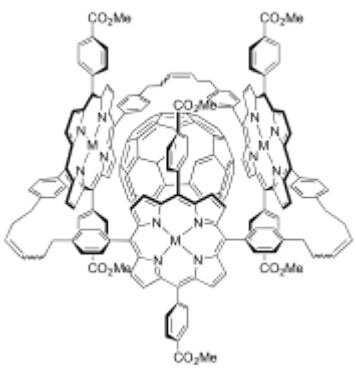
Disease Detection

Using genetic instruction materials such as DNA to probe sequences has implications not only for nanotechnology but also therapeutics for skin cancer and other disorders. Here we will be using fluorescently tagged peptide nucleic acids i.e. analogues of DNA in which the sugar-phosphate backbone has been replaced with an achiral (2-aminoethyl)glycine backbone. There are a number of advantages in using PNAs instead of oligonucleotides in antisense technologies, the major being their specificity and synthesis. In this project, you will be asked to design, synthesise and characterize PNA sequences containing fluorophores and to develop displacement assays to probe recognition.

Design, Synthesis and Application of New Macrocyclic Systems

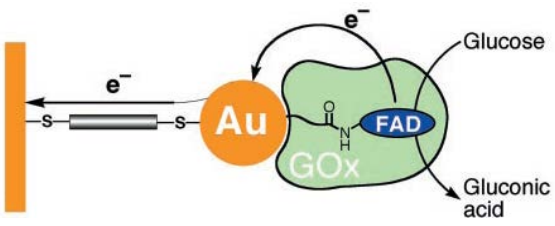


Novel container molecules with well-defined geometries have implications for a number of nanoscience-based applications based on their ability to include other molecules within their cavities and to order e.g. the calixarenes and cyclodextrins. Here, two projects are planned: (a) **A molecular square** (right) will be designed and constructed using pericyclic chemistry strategies and then once made, we will explore its molecular recognition properties with fullerenes and apply further functionalisation to produce porous materials. (b) **A multiporphyrin assembly** using olefination and template-directed approaches will be investigated in a second and independent project forming nano-sized molecular shuttles. This project builds on recent work within the group (*Chem. Commun.* **2011**, *47*, 1494-1496; *Org. Biomol. Chem.* **2012**, 6045-6053) and will involve functionalizing fullerenes as part of the project.



Fabrication of highly efficient enzyme electrodes for biosensor and biofuel cell applications (in collaboration with Jie Zhang and Alan Bond)

Direct electron transfer between an enzyme and an electrode is a practical problem that has attracted worldwide attention as a result of its impact in the areas of biosensors (e.g. glucose) and in biofuel cells to run, amongst other things, artificial hearts. An example of an enzyme electrode is shown below.



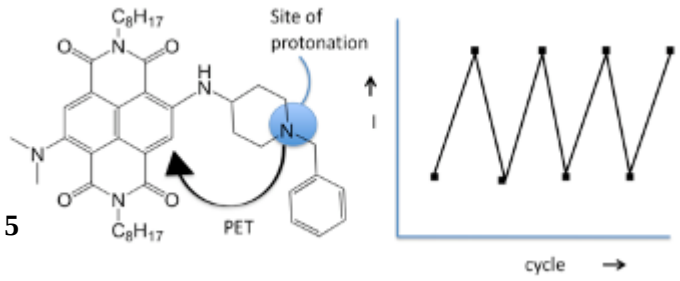
In an ideal world, direct electron transfer between an electrode and the enzyme is preferred, however this is currently not possible and mediators need to be used, which are impractical in an *in vivo* environment. The problems inherent to direct electron transfer between an electrode and large enzymes will be addressed by using electrodes modified with electronic and ionic conducting nanocomposite materials for enzyme immobilization. As one part of the electrode, these nanocomposite materials will work effectively as electron transfer relays to promote the direct electrochemistry of the enzyme.

In this project, students will be expected to carry out some or all of the following activities in order to understand the mechanisms of electron transfer processes involving enzymes:

- Synthesize novel nanocomposite materials including polymers
- Fabricate three dimensional enzyme electrodes using nanocomposite materials to promote direct electrochemistry of enzymes with high efficiency and high stability
- Study the electrochemistry

Synthesis and Properties of novel Naphthalene Diimides (in collaboration with Toby Bell)

The overall aim of our collaboration is to develop an innovative research program to evaluate a family of novel compounds that exhibit tunable fluorescent properties. Using these compounds, we will study energy transduction phenomena at the macromolecular, ensemble and SM levels. For proof-of-concept we will focus on applications including imaging, sensing, reaction kinetics and energy transfer processes.



5

Dr David W. Lupton

Room No. 238 Bld 23(S), Tel: 9902 0327, email: david.lupton@monash.edu

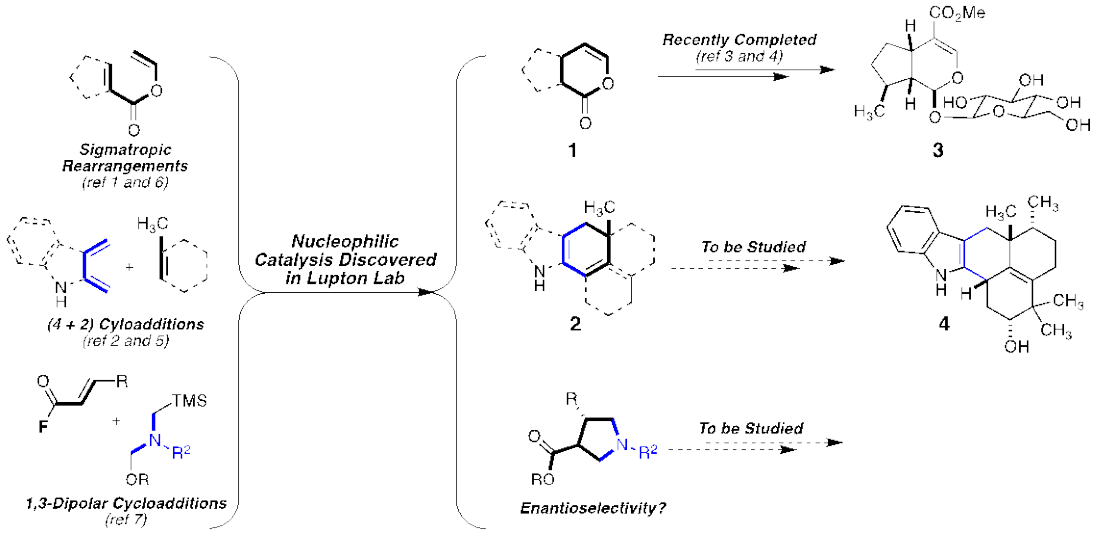
More information can be found at: http://users.monash.edu.au/~dwlupton/index.html in addition make an appointment to discuss chemical synthesis

Research in the Lupton group is focused on the discovery of new chemical reactions. We study ***organo- and transition metal catalysis*** and collaborate within Monash (Murray, Spiccia, Stasch and Thompson Groups) and North America to gain a deep understanding of ***how and why*** our reactions work. While all projects focus on chemical collaborative versions can be developed with a broader focus, these should be discussed with David.

Nucleophilic catalysis for the synthesis of pentacyclic indoles.

Nucleophilic catalysis is a highly active area of our group.[1-8] We have discovered a number of reactions that provide access to important structures found in medicinal agents and natural products (for example **1** and **2**).[1] These studies have recently led to the total synthesis of the β-glycoside iridoid **3**.[3-4]

In 2013 the honours project in this area involves extending the understanding of our recently discovered NHC catalysed (4 + 2) cycloaddition reaction,[2,5] and applying this reaction to the total synthesis of the antibiotic indole alkaloid **4**. In addition we have recently reported the first example of nucleophilic catalysis of a 1,3-dipolar cycloaddition,[7] while this reaction is successful modifications are required to allow this reaction to be enantioselective. You will develop new catalysts designed for this reaction.

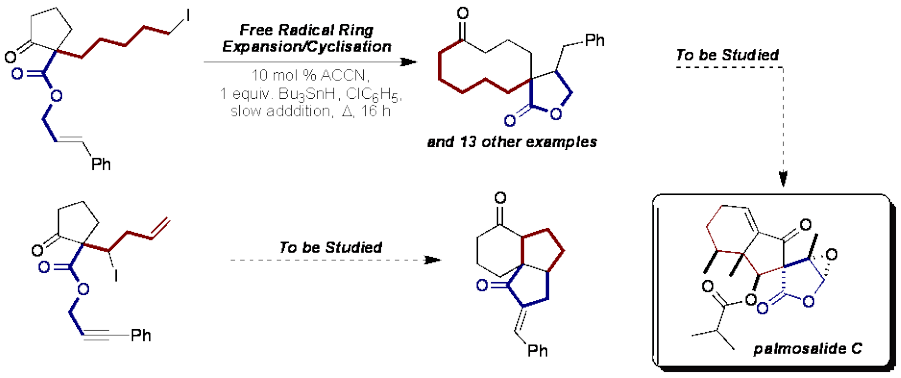


Scheme 1

1) Ryan, S. R.; Candish, L.; Lupton, D. W. *J. Am. Chem. Soc.*, **2009**, *131*, 14176;
2) Ryan, S. R.; Candish, L.; Lupton, D. W. *J. Am. Chem. Soc.* **2011**, *133*, 4694;
3) Candish, L.; Lupton, D. W. *Org. Lett.* **2010** *11*, 4836.
4) Candish, L.; Lupton, D. W. *Org. Biomol. Chem.* **2011**, *9*, 8182
5) Ryan, S. J.; Stasch, A.; Paddon-Row, M.; Lupton, D. W. *J. Org. Chem.* **2012**, *77*, 8831;
6) Candish, L.; Lupton, D. W. *Chem. Sci.* **2012**, *3*, 380;
7) Pandiancherri, S.; Ryan, S. J.; Lupton, D. W. *Org. Biomol. Chem* **2012** *DOI:10.1021/C2OB26047F*
8) For a mini review see Ryan, S. R.; Candish, L.; Lupton, D. W. *Synlett* **2011** 2275

Free Radical Reaction Cascade for the synthesis of palmosalide C.

In a new honours project for 2013 a student who wants a challenge is welcomed to a project that pushes the boundaries of radical rearrangement cascade chemistry. Recently we developed a rare example of a cascade Beckwith-Dowd ring expansion/cyclisation (Scheme 2).[9] This reaction uses materials that we have developed a range of techniques to prepare and manipulate.[10-11] In your project we extend these observations to develop a new radical cascade sequence that constructs three new rings in one-step (Scheme 2, second equation). In addition you will study the application of the former reaction (Scheme 2, first equation) to the synthesis of palmosalide C.

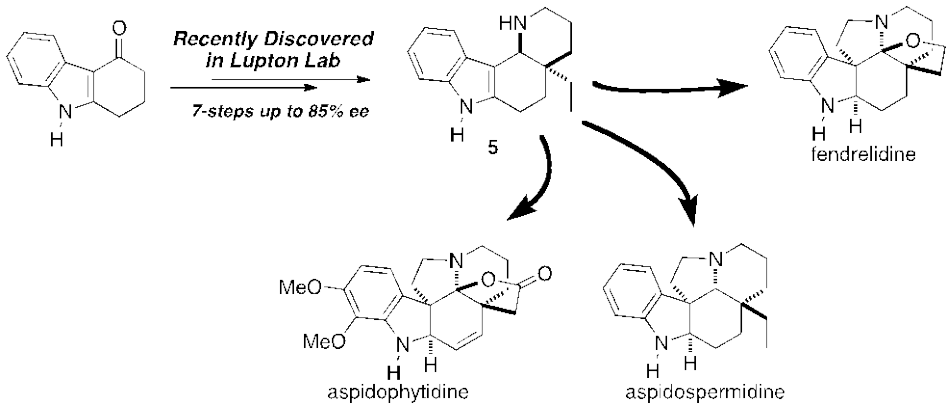


Scheme 2

9) Hierold, J.; Lupton, D. W. *Org. Lett.*, **2012**, *14*, 3412;
10) Hierold, J.; Hsia, T.; Lupton, D. W. *Org. Biomol. Chem.* **2011**, *9*, 783
11) Hierold, J.; Gray-Wealse, A.; Lupton, D. W. *Chem. Commun.* **2010**, *46*, 6789

Collective Synthesis using Pd-catalysis.

Transition metal catalysis has advantages over organocatalysis. Students in the Lupton group that work on this topic aim to exploit these strengths to develop new reactions useful for the assembly of challenging natural products.[12-13] Recent studies have uncovered a concise approach to tetracycle **5**, in 7-steps and excellent ee. In this project the honours student will exploit our capacity to easily access this intermediate to develop highly concise methods to access the natural products shown below.



Scheme 3

12) Gartshore, C. J.; Lupton, D. W. *Adv. Synth. Catal.* **2010**, *352*, 3321
13) Gartshore, C. J.; Lupton, D. W. *Under Review*

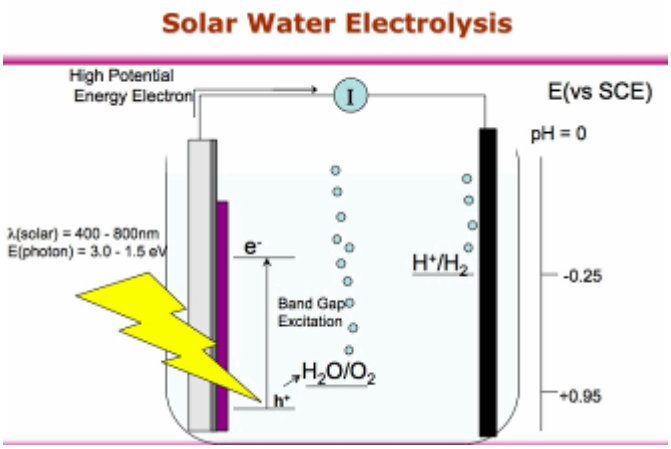
Professor Doug MacFarlane

Room No. 23/134, Tel: 9905 4540, email: **Douglas.MacFarlane@monash.edu**

This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me (details above). More information on my research can be seen at: ***www.chem.monash.edu.au/ionicliquids***

Hydrogen Generation from Solar Water Splitting (with Dr Alex Izgorodin)

Hydrogen is one of the ideal fuels for the future but needs to be generated in some sustainable way. Solar cells capable of directly splitting water into hydrogen and oxygen are one approach to this. The materials which support the photolysis of water are the key to a viable process. It is relatively easy to find materials which will work, but the challenge is to develop materials that will do so at high efficiency.

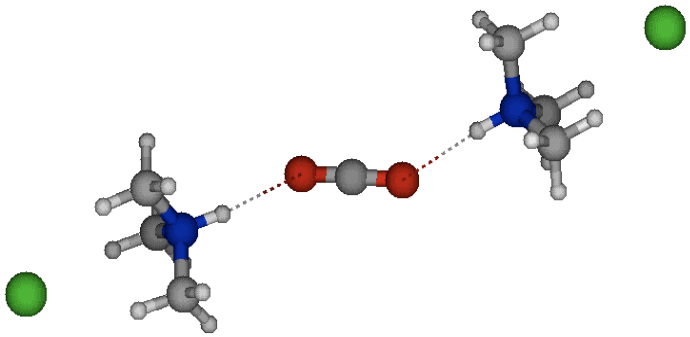


At Monash we are developing semiconductor materials capable of harvesting photons at wavelengths around 450nm and below.[1] .The project will expand this range of materials and test them in prototype cells to quantify their catalytic performance and lifetime. One of the key aspects of this is the interaction of the electrode material with the electrolyte and the project will investigate a number of electrolyte types. The project will suit someone with interests in materials or energy chemistry.

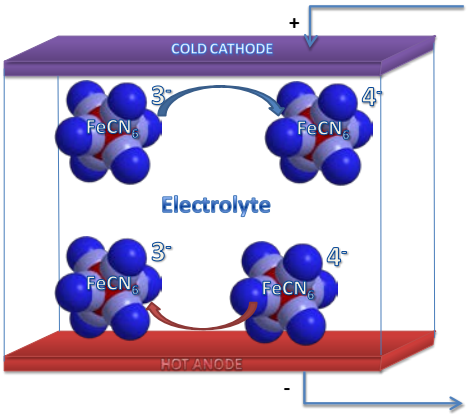
1. Izgorodin et al *Phys Chem Chem Phys* 2009

Ionic Liquids for CO_2 Capture (with Dr Vijay Ranganathan)

Ionic liquids (or organic salts which are liquid at room temperature) are being developed for a very wide range of applications. We are using ionic liquid concepts to develop systems for CO_2 capture in power stations. This project will investigate the properties of these compounds in this context and will suit a student with interests in synthesis, as well as physical properties. A student interested in combining this with computational studies could do so via our collaboration with Dr Katya Pas.



Ionic Liquids for Thermo-electrochemical Cells (with Dr Jenny Pringle)



Thermo-electrochemical cells are a new type of thermally activated battery that can capture waste heat from power stations and geothermal sources and produce a useful quantity of electricity. Fundamental to these is a redox couple and electrolyte that have strongly temperature dependent properties. Our PhD student Ted Abraham has recently discovered[2] a broad new family of complex-ion based redox couples that have superb properties in this regard and this project can involve both preparation of new variants of these and also the testing of them in cells.

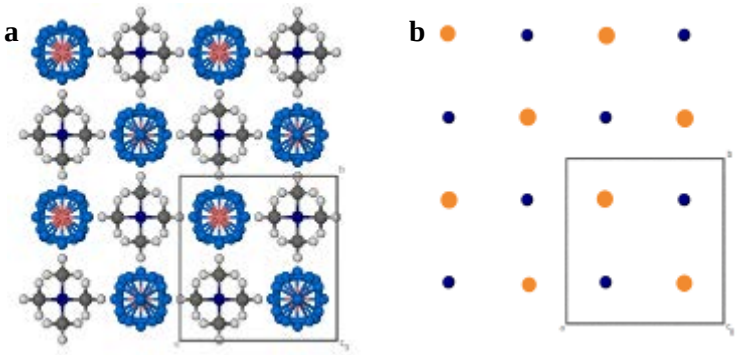
2. Abraham, et al. "Seebeck coefficients in ionic liquids -prospects for thermo-electrochemical cells", *Chem. Commun.* (2011).

Madelung Constants of Organic Salts (with Dr Katya Pas and Dr Pam Dean)

Recently we have solved the long standing problem of how to calculate the Madelung constant of organic salts.[3] This allows us to calculate the lattice energy of such compounds and hence understand their properties such as melting point, solubility, phase behaviour and so on. Unexpected transformation between different polymorphs is a major issue in pharmaceutical compounds.

This project can have synthetic, crystal growth, structure determination and/or crystal data base mining aspects depending on the interest of the student.

3. The Madelung constant of organic salts. Ekaterina I Izgorodina, Uditha L. Bernard, Pamela M. Dean, Jennifer M. Pringle, Douglas R. Macfarlane *Crystal Growth and Design* 2009.



Madelung Constant decomposition (right) of the crystal structure (left) of $Me_4N\ BF_4$.

Professor Philip Marriott

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Marriott Group homepage. **http://chem.monash.edu/staff/marriott/group.html**

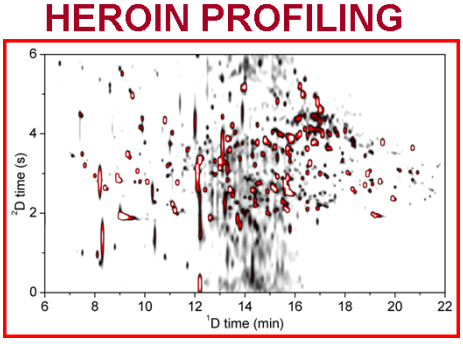
The Marriott Group specializes primarily in Analytical Chemistry, and specifically Separation Science / chromatographic methodologies hyphenated with mass spectrometry, and supported by a broad cohort of applications studies. In late 2012, we will take delivery of two triple quadrupole MS systems, and will have access to a Q-TOFMS; these will transform many of the studies that we can undertake, and with our MDGC research we can perform research that leads the world.

Our group has made significant contributions to the theory and practice of GC×GC. Both the GC×GC method, and fast MDGC approaches that we have pioneered, deliver much greater separation power – Informing Power – and improved sensitivity ~ these are the key requirements of any chromatographic method. Amongst our repertoire of applications we include petroleum, pesticides, essential oils, fatty acids, metabolomics, steroids, illicit drugs and other analyses. However, we appreciate that GC×GC is only one of the technologies through which GC plays a premier role in volatile chemical analysis. Recent developments include use of multidimensional methods to provide "complete resolution" of individual compounds from complex mixtures, then we use switching methods to direct flow (and hence the individual compound) to an external trapping assembly. In 2012, we have reported a completely new 'hybrid' GC×GC-MDGC method, which is able to completely extract specific compound chemical classes from within a complex sample, and a further capability that is able to generate GC×GC, MDGC, FID, MS data and olfactometry (sniff detection for aroma compounds) in the one integrated system.

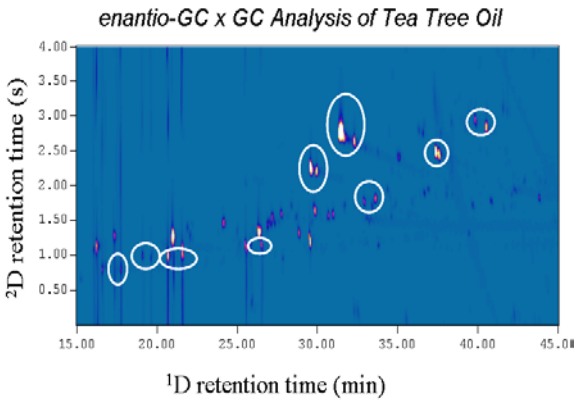
Illicit drug/doping control profiling using GC×GC & MDGC–Mass Spec technology

GC and HPLC are key tools for illicit drugs analysis. We have recently proposed new methods for drugs profiling based on the newly demonstrated capabilities of GC×GC. One of our key papers showed that we could apply this technology to analysis of the World Anti-Doping Agency (WADA) steroids, accomplishing levels of detection required by WADA for detection of key steroids in urine. However, rather than use selected ion monitoring (SIM) methods required in conventional GC, we use full scan mass spectrometry. We propose that this has many advantages for the routine analysis of drugs of abuse: (i) we get better spectral matching of the compound, and hence better confirmation; (ii) we have a 2D separation space that also aids confirmation of component identity; (iii) when full scan MS is used, we retain the full MS data of the experiment, to allow potential re-evaluation of the result should new designer drugs be discovered in future, and which may have been present in the sample. With our new triple quadrupole (QQQ) MS systems, we are in a position to significantly extend our capabilities to assess a range of contemporary analyses. We hope these provide a significant improvement in the deterrence of athletes from using drugs.

We have good experience in sports steroids analysis, and in late 2012, we will investigate beta-2 agonists, also a banned class of drugs during sports. For the present project we now wish to extend the method to other drugs on the WADA list, and this can include benzodiazepines, stimulants, and a variety of classes of compounds that are suited to GC analysis. We aim to add to the arsenal of analytical methods at the disposal of forensics and drugs analysts in the fight against doping.



Essential oils analysis: Coffee aroma / Chiral compound analysis using GC×GC and MDGC with cryotrapping and absolute structural identification



We will investigate the role of GC×GC and MDGC for chiral analysis, by using chiral-phase GC columns. The chiral column resolves enantiomers, and this project will variously apply chiral columns in the first and second dimensions to establish experience in this approach. Amongst other sample types, we are keen to study coffee aroma. By use of MDGC with a non-chiral/chiral column arrangement, we can select enantiomer compounds and resolve them on a ^{2}D column. The diagram demonstrates the use of a chiral ^{1}D column to separate pairs of enantiomers in GC×GC. In this case a chiral ^{2}D column is much less effective in separation.Use of preparative GC methods allows individual enantiomers to be collected, with further analysis by classical methods of circular dichroism and other spectroscopies. We have recently shown that it is possible to crystallize collected effluent from prep GC from repeat injections, and by use of X-ray methods, to achieve absolute chemical structural analysis. Whilst this is an ultimate structural characterization goal, demonstration of the basic method capabilities for chiral analysis will allow us to establish new technologies for enantiomeric compounds. By first establishing the appropriate sampling and analytical methods for general aroma analysis – and for this we like to use natural materials such as plant and coffee volatiles – we will then study enantioseparations using different GC methods as above, and develop advanced methods for absolute structural analysis. This study will be publishable.

The chemistry of thermal degradation of high temperature chemically bonded polymers: a model for GC stationary phase bleed

Project Description. One of the most pressing needs for gas chromatography is the production of thermally stable stationary phases that can adequately meet the demands of the thermal stress placed on them by the GC oven. The nature of the GC method is that we depend on the GC phase to provide appropriate separation towards sample compounds. We also do not want unfavorable thermal decomposition which can either reduce column lifetime, change the 'chemistry' of the phase, or its film properties. Phase bleed is commonly observed near the upper temperature limits of a GC phase. For instance, for a poly(ethylene glycol) phase, this is about 250-280 °C; for a 5% phenyl-methyl siloxane phase this can be up to 350 °C; for an ionic liquid phase the temperature limit can be variable. But most importantly, the actual degradation products are not well characterized. How is phase bleed recognized? We see phase bleed as a rising baseline on the detector (if it responds to the products of the degradation), and in general mass spectrometry suffers interference from bleed ions in the spectrum. This affects quality of MS data. For a siloxane phase, bleed ions 207/281 m/z are common. Such phases generate compounds called D3, D4 and D5, corresponding to cyclic compounds, as shown here. But the different kinetics, and a thorough analytical study does not appear to have been conducted. We have developed an approach that we call targeted cryogenic modulation that we anticipate will be able to provide resolution of many degradation products of phase polymers. We also have a wide range of GC columns available. We aim to conduct a systematic quantitative and qualitative study of phase bleed, with GC-MS and GC-QQQMS. We will also seek to conduct an industry-wide study by proposing our study to major GC column manufacturers, as the first benchmarking effort to characterize GC columns. The outcome should be provide a basis upon which column preparation processes can be contrasted and optimized. This study will be publishable.

Associate Professor Lisa Martin (only collaborative projects in 2013)

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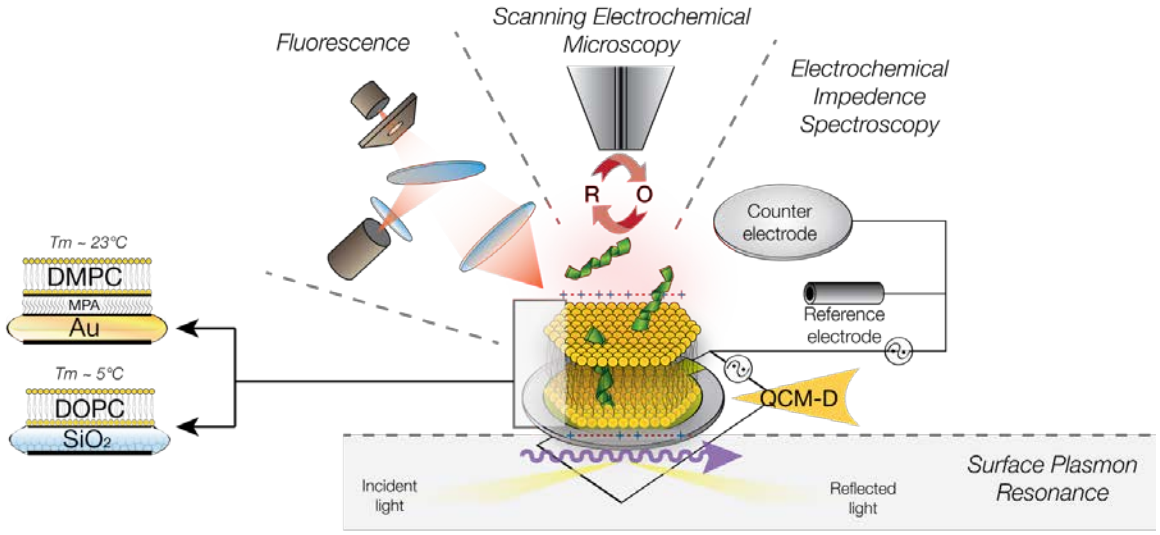
More information on our research can be seen at: ***www.chem.monash.edu.au/staff/martin/***

Our research explores the chemistry behind **Biology and Medicine.** This involves small molecule synthesis 'bottom up' and larger biomolecular studies of proteins and peptides. We probe the structure, function and reactivity of biomolecules that achieve highly specific and selective chemical transformations *in vitro*. These molecules can be used for biotechnological devices, eg. synthetic reactors or biosensors.

We aim to explore chemical biology using a combination of biophysical methods (see Figure);



Our multi-disciplinary approach includes; synthesis, small molecule characterization (NMR, UV-visible, IR, LC-MS) through to more bioanalytical methods, such as, protein electrochemistry, Quartz crystal microbalance (QCM), Surface plasmon resonance (SPR), fluorescence and Atomic force microscopy (AFM). Some general project areas are:

- *Cytochrome P450 biocatalysis* – redox biosensor development,
- *Protein regulation of prostate cancer* – allosteric control of protein function,
- *Antimicrobial and cell-penetrating peptides* – elucidation of membrane-peptide activity,
- *Insulin family peptide-receptor activity* – molecular basis for activation and signaling,
- *Charge-transfer and molecular movement across membranes* – ion channels, secretion,
- *Biocomputers* - Semi-conducting biomaterials based on biomolecule charge-transfer complexes

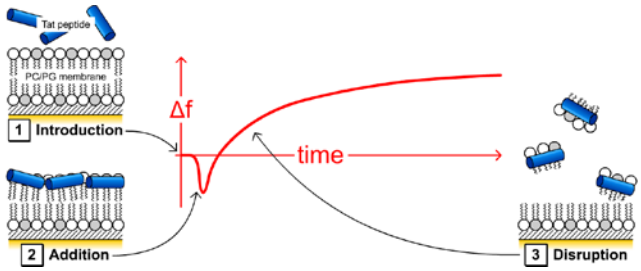
A number of these projects involve collaborations with colleagues within the School of Chemistry, other faculties at Monash or with national and international colleagues.

Some selected projects are shown below:

Membrane-penetrating peptides (with Toby Bell)

Membrane-active peptides include cell penetrating (CPP) and antimicrobial (AMPs) peptides. These two classes of peptides provide a wide spectrum of peptide mechanism and activity towards membranes. The increase in multidrug-resistant bacteria has provided an imperative for antimicrobial peptides to be considered as drugs and treatments. These AMPs are a promising solution because they are generally selective for bacterial membranes; they have broad-spectrum

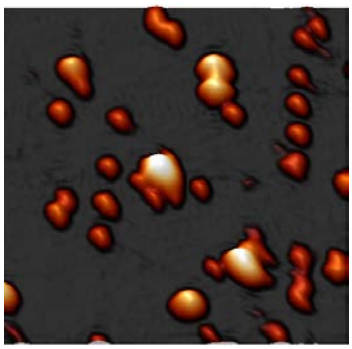
antibacterial activity again Gram-positive and negative bacteria, fungi, parasites, viruses and even have anticancer activity. Also, they do not induce resistance compared with conventional antibiotics. More than 800 naturally occurring AMPs have been isolated containing various sequences and thousands of synthetic derivatives are known. In contrast, CPPs have been widely used to transport cargo inside cells for biomedical applications, although some eg. penetratin also have antimicrobial activity. Cargo can be attached readily to the peptide using a redox sensitive probe eg. a disulfide linker such that dissociation occurs in the reducing cytosol. Structurally, these membrane-active peptides have little in common, although many are cationic and amphipathic. However, mechanistically a number of possible pathways for peptide-membrane interaction have been suggested: the major pathways for AMPs being; peptide accumulation parallel to the membrane surface to disrupt the membrane by the carpet mechanism or by self-association of the peptides to form pores within the membrane layer. In addition, CPPs can act by endocytosis or directly by translocation of the membrane – observed using a trans-membrane potential.



Membrane disruption by the Tat peptide from the HIV virus. The Quartz Crystal Microbalance Δf-t trace.

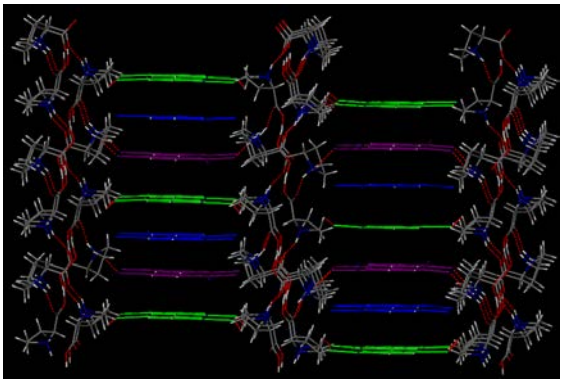
Structure and morphology of cytochrome P450 proteins (with Dr. Rico Tabor)

Atomic force microscopy can provide molecular resolution images of biomolecules, allowing us to explore the three-dimensional arrangement of proteins in liquid. Structural information including conformational and dynamic association with other molecules can be obtained for direct comparison with functional studies. This project will use AFM as the primary technique to investigate the morphology of proteins in solution and on biomimetic surfaces. Complementary biophysical and biochemical studies of these proteins will allow us to understand the influence of surfaces on the ability of the protein to function, by converting substrate into product.


AFM of cyt P450c17 on lipid

Designer Biocomputers – biomolecular semiconductors (with Prof. Alan Bond)

Novel semiconductors can be prepared using L-amino acids that form charge-transfer complexes with the TCNQ (7,7,8,8-tetracyanoquinodimethane) anion. We have prepared the first amino acid TCNQ complex and as seen in the X-ray crystal structure of this biomaterial it has a sophisticated three dimensional H-bonding structure in which the semiconducting properties arise from the π-stacking of the TCNQ units. This project offers the chance to explore other biomolecular derivatives with TCNQ ([bio-cation][TCNQ]). The combined amino acids with TCNQ to form quasi-one dimensional charge-transfer nanostructures offer the opportunity to develop new materials with intriguing properties and biocompatibility. This project offers enormous scope and the chance to develop physicochemical skills in SEM, SECM, AFM, X-ray crystallography and molecular computing.


X-ray crystal structure of the amino-acid Proline biomaterial which is semi-

Professor Don McNaughton, Dr. Chris Thompson and Dr. Dominique Appadoo (Australian synchrotron)

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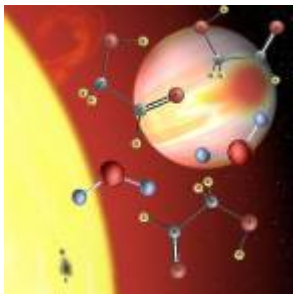
High resolution spectroscopy of atmospheric species, transients and interstellar molecules.

High-resolution FTIR spectroscopy has applications in:

- Atmospheric monitoring
- Molecular dynamics
- Elucidation of molecular structures and molecular interactions
- Interstellar and planetary chemistry



Our high resolution infrared and microwave spectroscopy laboratories are well equipped with multipath cells, jet expansion cooling and pyrolysis equipment, which together allows us to tackle a number of problems in the areas listed above. One of the areas of interest where we have already carried out a number of projects is the generation and study of short lived species. The Australian synchrotron provides an added advantage for this work with a new source providing an extremely spectrometer coupled to the bright synchrotron In 2013 we will concentrate on sensitive research tool. importance in the interstellar obtaining and assigning spectra of species of that will help our understanding of medium with a view to providing information work may involve experiments at the the interstellar medium. A large part of this possible to combine a microwave Australian synchrotron. In 2013 it may also be spectroscopy study.

Far and mid Infrared synchrotron spectroscopy of aerosols

Much of the information on aerosols in the atmosphere (earth and planetary) and on interstellar "dust" comes from far and mid infrared spectroscopy. This project will explore the IR spectroscopy of aerosols generated at low temperatures in a collisional cooling cell with a view to characterizing and understanding "models" of interstellar dust and planetary aerosols. At the synchrotron our cell is currently under modification to allow for uv radiation of the species generated to enable us to monitor the chemistry of such these model systems.

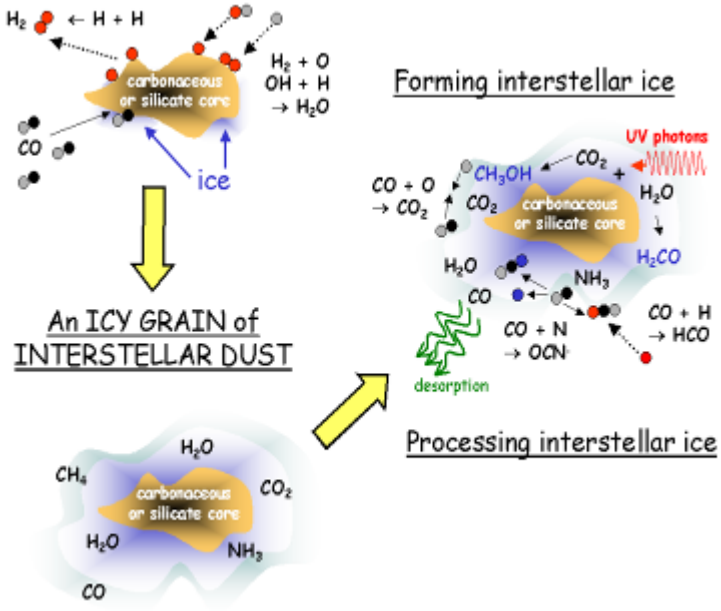
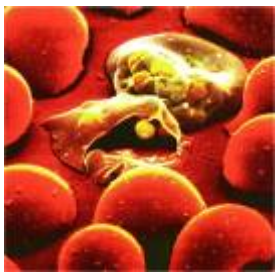


Figure 1: Interstellar dust grains are thought to consist of a silicate or carbonaceous core surrounded by a 'bulky' molecular ice layer, typically 20 nm in diameter.

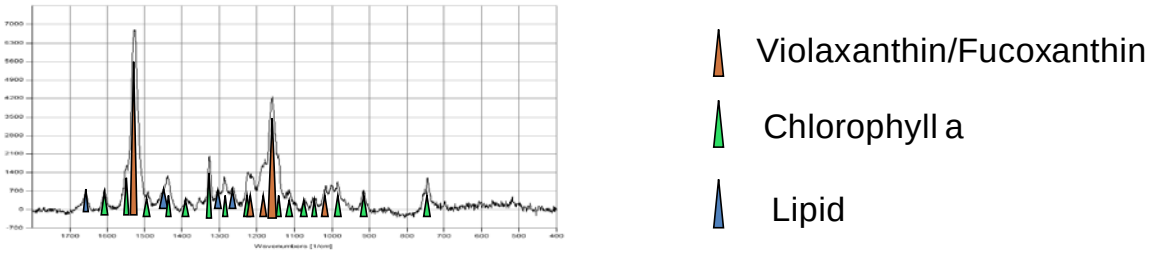
Microspectroscopy of *chromera velia*, a prospective malarial drug model organism.(with Prof John Beardall)



The malarial parasite *Plasmodium falciparum* contains an unpigmented chloroplast remnant termed an apicoplast which is a target for malaria treatment. Recently a very close relative, *chromera velia*, with a photosynthetic plastid has been found (Nature 452, 959 (2008)). This organism provides a powerful model with which to study parasitism and is a potential model for the study of antimalarial drug interactions. This project, carried out with Dr. Dee Carter, University of Sydney, will explore Raman, uv-vis and infrared micro-spectroscopy and imaging as techniques for chemically characterizing this organism, spatially locating the plastid and understanding how the organism and its chemistry develops under varying conditions. *Chromera velia*, will be cultured in Biological sciences under different growth conditions and the spectroscopic results will be compared with Pulse Amplitude Modulated *Fluorometry*.

Infrared and Raman Microspectroscopy to monitor biodiesel production.

Microalgae that produce high quantities of lipid are being investigated as potential sources of biofuels with laboratory scale pilot plants operating. Current methods for chemical analysis and optimization of the growth conditions are extremely slow and laborious and this project is aimed at developing spectroscopic techniques to rapidly determine lipid type and lipid, carotenoid and chlorophyll concentration, for small numbers of algal cells or single algal cells.



Raman spectrum of a single 2 micron diameter microalgal cell.

Professor Keith Murray

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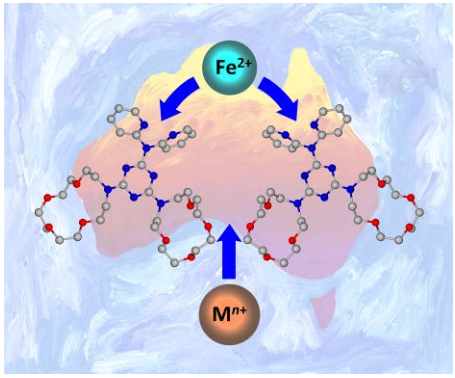
This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me

More information on my research can be seen at: ***www.chem.monash.edu.au/staff/murray.html***

Synthesis and Magnetostructural Investigations of Mononuclear and Polynuclear Spin Crossover Compounds of Iron and Cobalt

(Co-Supervisor: Dr. Stuart Batten)

Spin crossover centres are a well-known form of an inorganic electronic switch, for which a variation of temperature, pressure or light irradiation leads to a change in d-electron configuration (high-spin to low-spin) often accompanied by a change in structure, colour and magnetism. We aim to synthesise and study a wide variety of novel spin crossover metal complexes where cooperativity between centres, induced by careful supramolecular design, will lead to molecules and materials having memory retention, magnetic spin-coupling and/or microporosity. The significance of these aims covers several fundamental questions in the science of electronic nano-magnetic systems. Future applications of such materials are in "switchtronic" materials.
Hayley Scott and Caspar Schneider (PhD students), Drs Ian Gass and Victor Martinez (Postdoctoral Fellows) are currently extending our study of spin crossover and supramolecular systems of the cluster and 1D types, including Fe and Co –organic radical systems. Dr Tamsyn Ross's work (PhD 2011) has been published including an invited front cover for *Dalton Trans.* (below). The choice of ligand and/or their substituents are of paramount importance in obtaining spin crossover behaviour, so that organic synthesis as well as metal complex synthesis is involved in this project.

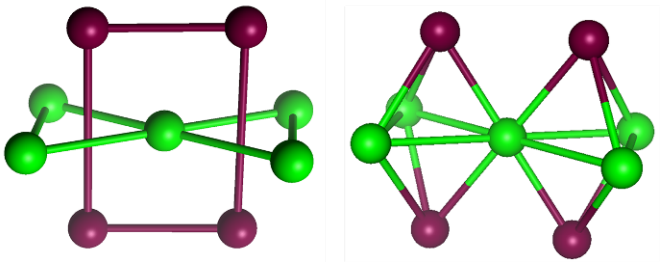


This project is aided by the support and collaboration within the Murray and Batten Groups, notably Dr Boujemaa Moubaraki ("Squid" Magnetism) and Associate Professor John Cashion (Mössbauer spectroscopy - Physics Department. We have a collaboration on photomagnetic studies with Prof. Jean-François Létard (Bordeaux, France) and Hayley and Victor will do studies in Bordeaux in Sept 2012. With Dr David Turner's help, synchrotron crystal and powder diffraction studies are made, across the road, at the Australian synchrotron. Dr Suzanne Neville collaborates on nanoparticle spin crossover work, structure and and synthesis.
The ligands and resulting metal compounds, for Project 1 and Project 2, below) will be characterized and further investigated using a variety of techniques including IR, mass Spec., UV-Vis, microanalyses, X-Ray crystallography, NMR (^{1}H & ^{13}C), magnetism and Mössbauer spectra. The precise level of involvement of these techniques will depend on the interest of the student.

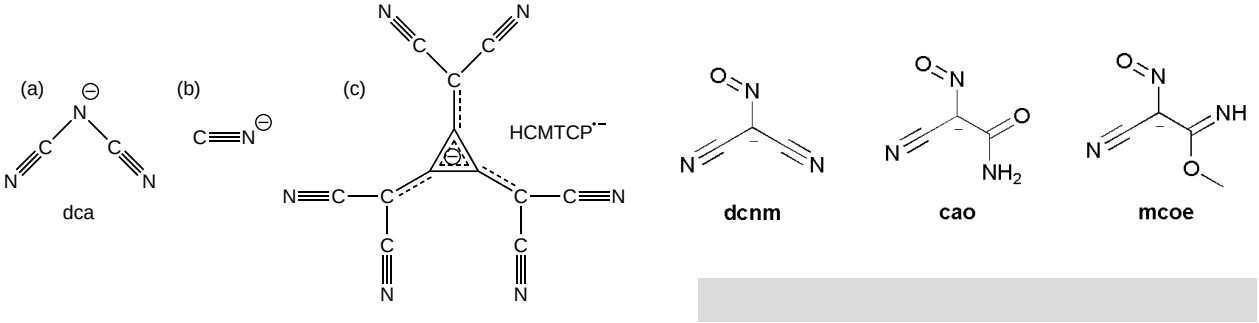
Synthesis, crystal structures and physical properties of 'spin-coupled' Mn, Fe and M-Ln 'metallosupramolecular' cluster compounds and of metal-coordination polymeric materials.

(Co-Supervisor: Dr. Stuart Batten) see also project with Dr Suzanne Neville.

(a) The first project is to synthesise new, large clusters of Mn, in mixed oxidation states, and of f-block-only or mixed d-block/lanthanide combinations, that display "quantum effects" (single molecule magnets, SMMs); with possible future uses in "spintronics"/molecular computers). Dr Stuart Langley (Post doc), Dr Ian Gass (Post doc) and Nick Chilton (R.A.) are successfully using ligands such as $N(CH_2CH_2OH)_3$ to make a range of beautiful clusters with very interesting properties. We collaborate with Dr Rajaraman, India, on theory. A "bow-tie" Cu_5Ln_4 cluster (below left) has shown fascinating SMM magnetism and magnetic refrigeration (Ln = Gd) properties (*Chem Sci.* 2011, **2**, 1166; *Chem. Eur. J.* 2011, **17**, 9209)



(b) The second is to make new examples of polycyano-bridged metal frameworks and clusters, including lanthanide species, using the ligand types shown below, studied by David Turner (Future Fellow) and Rizal Razali (PhD student) (a recent review is in *Chem Comm* 2011, **47**, 10189 and a Dy_8 paper in *Dalton Trans.* 2012, **41**, 3751):



Dr C. André Ohlin

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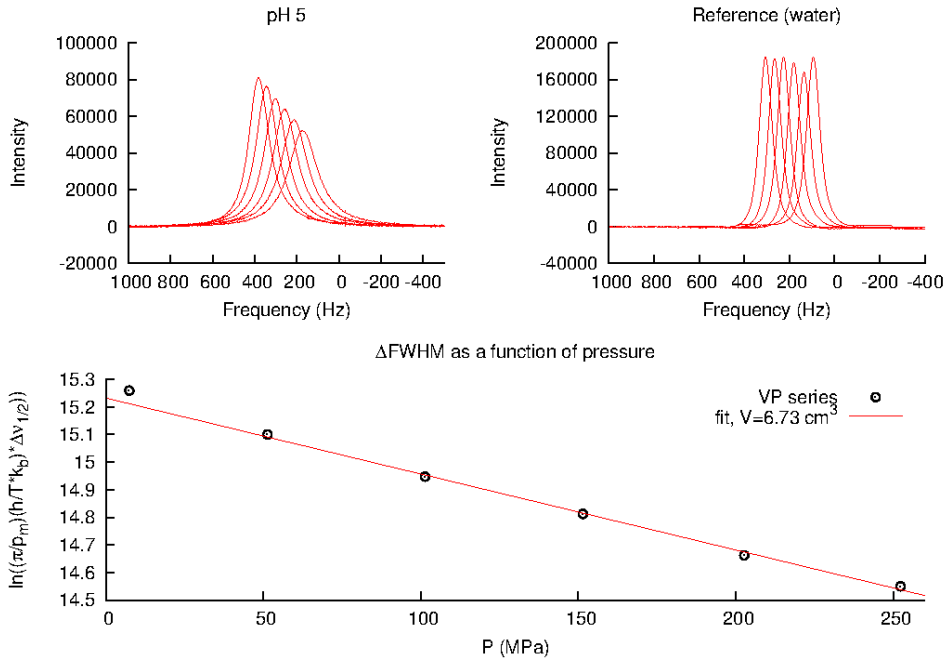
More information on our research can be seen at: ***www.chem.monash.edu.au/staff/ohlin.html***

Rates of exchange of carbon dioxide on transition metal complexes

The conversion of carbon dioxide into more complex molecules constitutes one of the corner stones of C1 chemistry, and is a process which is familiar to all of us in the form of photosynthesis. On a more modest scale, carbon dioxide can be converted into formic acid, formaldehyde, methanol and methane via stepwise reduction using transition metal catalysts.

We are interested in the interaction between transition-metals and carbon dioxide/carbonate and study this interaction using primarily NMR methods. Depending on the metal, this interaction can be followed by line-broadening (paramagnetic metals) or by saturation transfer (diamagnetic metals).



Above: Line-broadening of the water signal of a cobalt solution as a function of pressure.

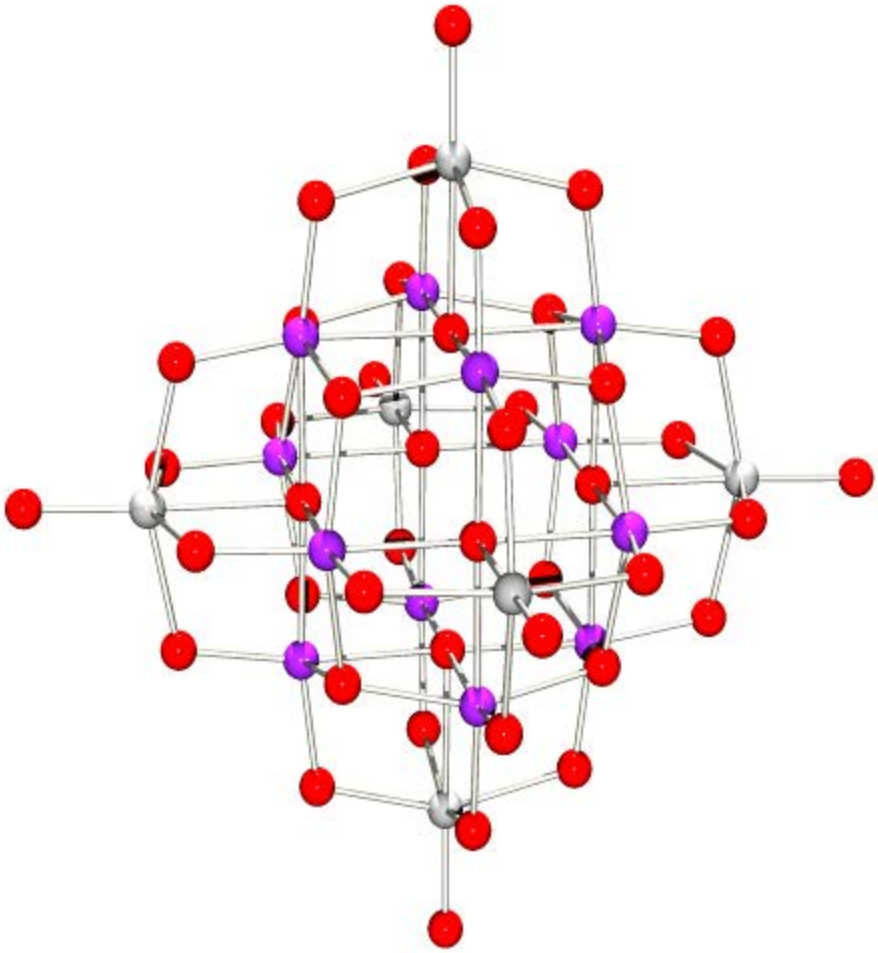
The project will consist of the synthesis of well-defined metal-aqua complexes using literature procedures, characterisation of the complexes as a function of pH using potentiometry and spectroscopy, and determination of rates of ligand exchange by NMR. In addition, we use basic NMR theory and simulation to predict and understand our observations.

Exploration of the chemistry of polyoxoniobates

Polyoxometalates (POMs) – discrete oxide clusters of the group V and VI elements in their highest oxidation states – make up a field which has been gaining increasing attention over the past 15 years. While V, Mo and W polyoxometalates have been investigated in some detail, very little research has focused on the Nb and Ta polyoxometalates. Recent research has shown that the chemistry of these polyoxoniobates and -tantalates is a lot more complex and extensive than previously thought. This is exciting, as Nb and Ta POMs tend to be stable at a higher pH than V, W and Mo POMs – pH where carbon dioxide is highly soluble in the form of carbonate. In addition, their high oxidation state may make them suitable as temporary electron sinks, making

Nb and Ta POMs an interesting proposition as ligands in reductive catalysis, such as carbon dioxide/carbonate reduction.

The project will consist of two main parts: 1) the synthesis of new polyoxoniobate clusters by tuning synthetic conditions, in particular pH, and 2) the synthesis of complexes of polyoxoniobates and other transition metals.



Above: The $[Ti_{12}Nb_6O_{44}]^{10-}$ ion was only discovered in 2008.

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Prediction of viscosity in imidazolium-based ionic liquids (with Prof. Douglas MacFarlane)

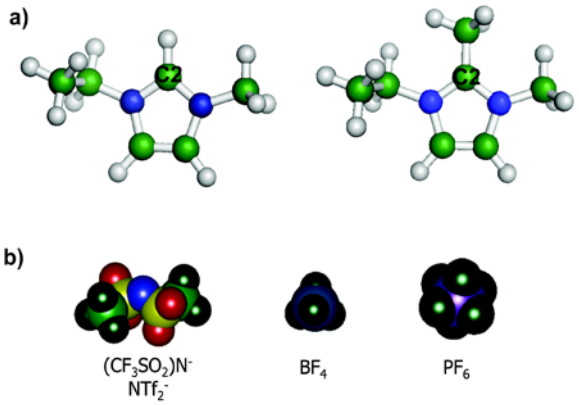

Figure 1. Structure of a) imidazolium-based cation and b) weakly coordinating anions

Ionic liquids (ILs) belong to a fascinating class of compounds that comprise entirely of ions. The interest in ionic liquids has been growing ever since they were introduced due to their unique properties such as high conductivity and low melting point. Imidazolium-based ILs (see Fig. 1a) tend to have lower viscosity and higher conductivity. Replacement of the hydrogen atom by a methyl group in the C2 position drastically changes transport properties, especially viscosity. Recently we investigated potential energy surfaces (PESs) of the anion moving around the imidazolium cation and showed that the increase in viscosity was associated with the decreased mobility of the ions due to significantly increased transition barriers on the PES between ion-ion conformations. The aim of this project is to apply the same approach to a number of weakly coordinating anions (see Fig. 1b) and calculate transition barriers and hence, predict viscosity of these imidazolium-based ionic liquids. The student will learn how to use quantum-chemical packages such as GAMESS-US and TURBOMOLE. This project will be done under the ARC Discovery project entitled "Fully *ab initio*, large-scale calculations of thermodynamic and transport properties of ionic materials".

Development of new electrolytes for lithium-ion batteries and solar cells

Traditional molecular solvents such as acetonitrile and ethylene carbonate are widely used as electrolytes in metal-ion batteries, solar cells and fuel cells. For example, smart phones such as iPhone operate on rechargeable lithium-ion batteries. It has become quite common that these batteries do not last longer than two years because of corrosion and volatility issues associated with traditional electrolytes. Ionic liquids (ILs) are considered replacement electrolytes due to their unique properties such as inert nature and negligible vapour pressure. Although possessing many desirable properties, ILs are usually more viscous than molecular solvents, thus limiting their applicability as electrolytes in electrochemical devices. The best way to decrease viscosity of ILs is to mix them with molecular solvents, although this result might also come at the expense of decreased conductivity. These mixtures represent potentially viable electrolytes without drastic changes to the currently existing techno-logies. Recently we showed that the Fragment Molecular Orbital (FMO) approach

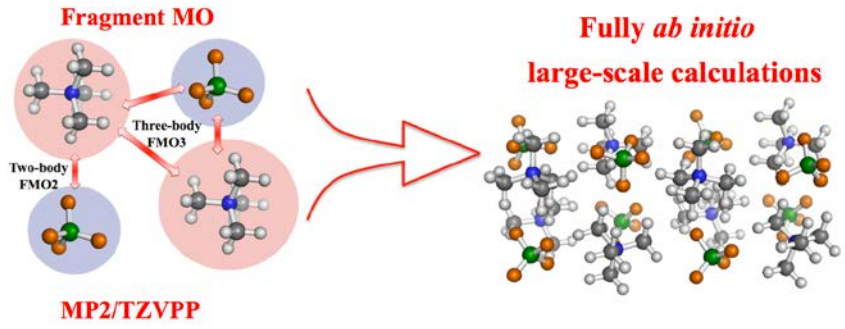

Figure 2. The Fragment Molecular Orbital approach in the nutshell

combined with the MP2 level of *ab initio* theory (see Figure 2) was a powerful method to accurately study energetics of ionic clusters consisting of a number of ionic liquid ions. (*Chem. Commun.*, 2012, **48**, 1493). Coupled with the molecular dynamics (MD) approach, this *first principles* approach provides an excellent opportunity to study structural arrangement and transport properties of mixtures of ILs mixed with molecular solvents. This project aims at performing FMO-MD simulations of ionic liquids coupled with ethylene carbonate and acetonitrile to design novel mixed electrolytes that have low vapour pressure together with low viscosity and high conductivity. The student will learn how to use computational packages, GAMESS-US and CHARMM, and will perform FMO-MD calculations at the Monash *e*-research Centre. There is a possibility of testing the selected electrolytes with desirable properties in the laboratory. This project will be done under the ARC Future Fellowship entitled "Towards *ab initio* molecular dynamics simulations of proton and electron transfer processes".

Prediction of reduction potentials of metal ions in ionic liquids

Figure 3. Examples of industrial electroplating of metals

Electroplating of metals is a widely used industrial process for coating metal objects with a thin layer of a different metal, making them more durable and corrosion resistant. The objects include anything from house keys to parts of computers, cars and aircrafts. Electrodeposition, a process of electroplating, is usually done from an aqueous solution of metal salts at high temperatures. Aqueous solutions have a narrow electrochemical window, limiting electrodeposition of metals such as Al, Ti and W with reduction potentials below -1.23 V. The aluminium and titanium metals are of particular interest in airspace and marine industry due to their high corrosion resistance. Ionic liquids can be designed to be electrochemically stable and thus have much wider electrochemical windows compared to water (see Figure 4). The other advantage of ionic liquids arises from unique speciation processes between IL ions and metal cations, resulting in a decrease of reduction potentials of metal ions and allowing for electrodeposition of metals at lower reduction potentials and lower temperatures. This project aims at predicting reduction potentials of industrially important metal ions such as Al^{3+} and Ti^{4+} from ionic liquids *from first principles*. The FMO-MD simulations described above will be performed to monitor the speciation mechanisms of metal ions upon the metal ion reduction in a number of ionic liquids. This approach will allow us to select ionic liquids that help reduce the reduction potentials of metal ions without significant changes to transport properties of the ionic medium itself. The student will learn how to use computational packages, GAMESS-US and CHARMM, and will perform FMO-MD calculations at the Monash *e*-research Centre. There is a possibility of testing the selected ionic liquids for electrodeposition of Al and Ti in the laboratory. This project will be done under the ARC Future Fellowship entitled "Towards *ab initio* molecular dynamics simulations of proton and electron transfer processes".

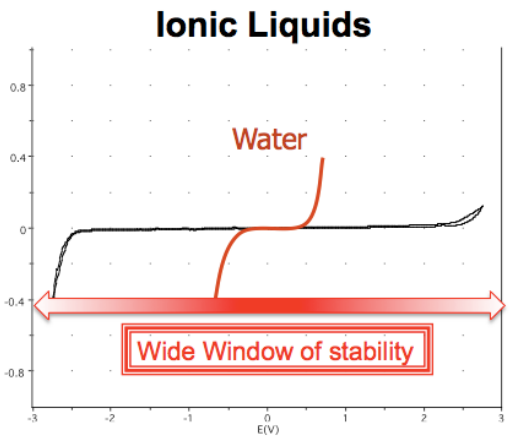

Figure 4. Comparison of electrochemical windows of ionic liquids (black curve) and water (red curve).

Associate Professor Tony Patti

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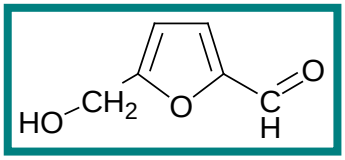
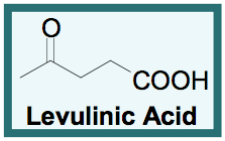
Soil Organic Matter, Soil Carbon Sequestration, Humic Substances and Soil Fertility (with Dr Tim Cavagnaro (Biological Sciences), Prof Roy Jackson and Prof Alan Chaffee)

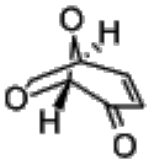
Understanding the role and dynamics of soil organic matter in soils is critically important in maintaining soil fertility, water retention and nutrient cycling. It also plays an important function in the long-term sequestration of carbon. Soil organic matter can come from photosynthetic processes or added organic amendments such as composts, coal products (including humic preparations) and crop residues (e.g. stubble, mulches and agrichars)
The potential benefits of organic amendment applications to soil include reduced greenhouse gas emissions, increased C sequestration, reduced fertilizer and water requirements, improved soil fertility and increased crop production. This area of investigation allows a number of projects to be undertaken. These include: an evaluation of selected amendments on soil physicochemical, biological properties and soil enzyme activities; fertilizer potential of nutrient enriched biochars; chemical composition of litter inputs in forested areas and its decomposition/transformations in soil. Soil-plant interactions in the presence of selected amendments can also be explored through plant growth experiments for those interested. These projects are ideally suited for anyone interested in combining chemistry and biology in the area of soil science.

Fine chemicals from Biomass Waste (with Profs Roy Jackson and Doug MacFarlane)

The use of biomass to derive fine chemicals and fuels has been gaining momentum and is the subject of growing research efforts. The processes we have been investigating generate several key compounds including:5-hydroxymethyl furfural, levoglucosenone and levulinic acid.







5- hydroxymethyl furfural

levoglucosenone

This project will examine several biomass waste streams (e.g woodwaste, algae) and evaluate their potential for producing valuable chemical feedstock compounds. Reaction conditions and catalysts to optimise product yields will be explored. An investigation into the chemistry of levoglucosenone can also be undertaken for students interested in organic transformations.

Use of Ionic Liquids for Selective Extraction of Soil Organic Matter and Biomass (with Profs Alan Chaffee and Doug MacFarlane)

Ionic liquids offer potential for the selective extraction of particular fractions of soil organic matter and biomass, including lignocellulose, proteins, humic substances and other classes of organic matter. For example, fundamental studies on the nature of soil organic matter require novel extraction techniques and fraction into different classes of material.

Managing Winery Wastewater and other wastewater streams through combined Catalytic and Biological approaches (with Dr Tim Cavagnaro (Biological Sciences) and Prof Leone Spiccia)

The evaluation of and cost-effective treatment of wastewater from different sources continues to provide a challenge for many industrial sectors. The wine production industry, for example, generates large amounts of wastewater. Often these wastewater streams could be treated at their source and used in the same locality (e.g on pasture and other crops). Rapid biological evaluation (for plant toxicity) and simple treatments can offer the most effective and economical outcomes for wastewater re-use. The development of benign catalysts that decompose organic contaminants, pollutants, and harmful microorganisms is needed for various applications including water purification. Both photocatalysts and redox catalysts have been used independently, but there are fewer examples which combine both activities. The most-commonly used photocatalyst is titanium dioxide, TiO_2, while redox catalysts include manganese and cerium oxides. This project will attempt to synthesise and characterise oxides which combine both photo and redox catalytic properties. These will be tested against a range of common classes of organic pollutants and evaluated for plant toxicity and effects on soil.

Dr Kei Saito

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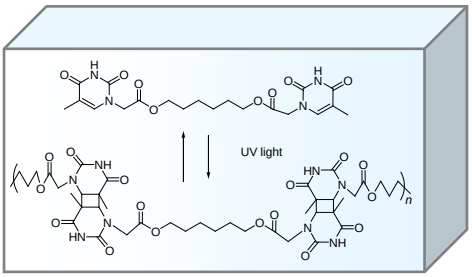
Green Material Chemistry

Green chemistry is an academic field in chemistry that is concerned with the design of safe processes and products. Our projects will focus on developing new synthesis and production methods for novel sustainable/environment benign materials based on the principles of green chemistry by understanding naturally occurring mechanisms that can be extrapolated to synthetic systems using polymer, supramolecular, catalyst, and nano chemistry.

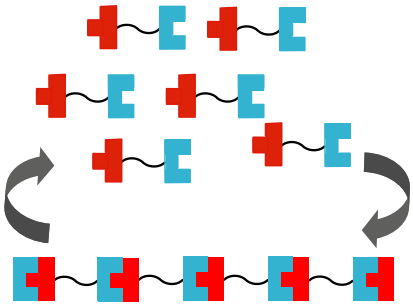
More information on my research can be seen at:http://www.chem.monash.edu.au/staff/saito/

Developing a Novel Polymer Recycling System

Solid-Crystalline Photoreversible Polymerization

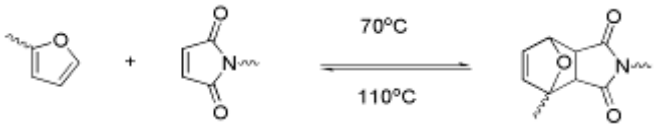


Thymine, one of the nucleic bases in DNA, features both the ability to form relatively strong hydrogen bonds as well as the ability to photocrosslink. Photocrosslinking of thymine occurs when irradiated > 270 nm UV. Crosslinking is reversed either by irradiation at < 249 nm UV or enzymatically. By using these mechanisms, thymine functionalized monomer can be photopolymerized and photodepolymerized. We will study the formation of crystals from alkyl bis-thymine derivatives and their solid state photopolymerization (topochemical polymerization) and photodepolymerization.[1] This project will provide novel polymerization methods and also a novel polymer recycling method using the principles of green chemistry. Honours project in this area will involve the synthesis of bis-thymine derivatives synthesis and its characterization in crystalline state.

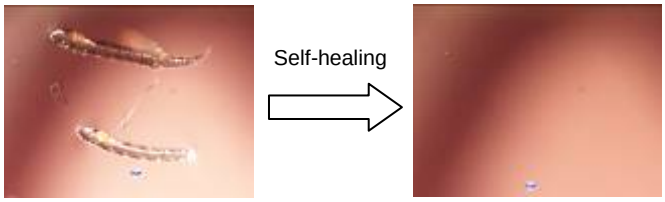


1. P. Johnston, C. Braybrook, K. Saito, *Chemical Science*, **2012**, *3*, 2301–2306.

Self-healing Polymers (Co-Supervisor: Prof. George Simon, Material Engineering)

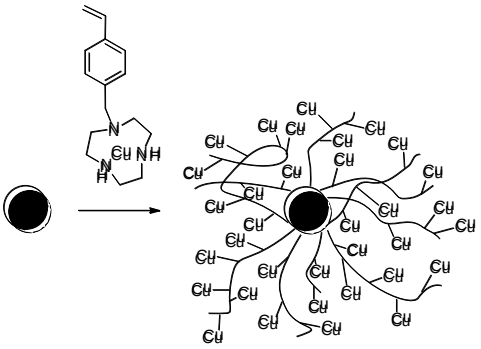


Polymers have a number of applications in many fields because of their outstanding properties and are becoming indispensable in modern life. However, under high stresses and strains often seen in service, polymers have a finite lifetime and can often fail. Sometimes this failure may not be complete failure, but be cracks or points of weaknesses in larger structures. In these cases, it would be desirable that polymers have self-healing properties, as do animals and plants. Some strategies like autonomous mending and external stimuli mending have been researched to make the thermo self-healing polymers. One of the ways to produce self-healing polymers is to incorporate reversible units such as Diels-Alder units in polymer structures. We will investigate thermal self-healing epoxy and acrylic resin using furan-maleimide Diels-



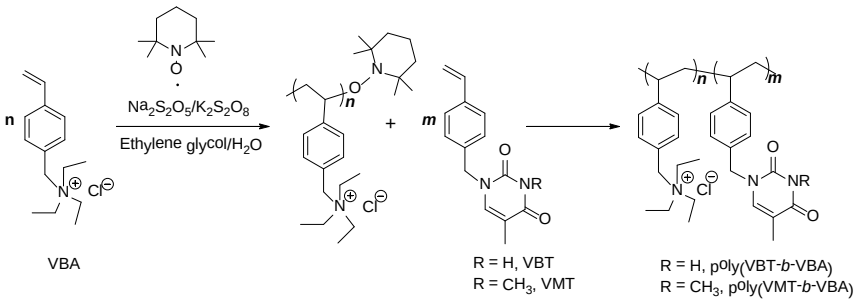
Alder cross-linkers. This project will involve aspect of organic synthesis, polymer synthesis and polymer characterization techniques.

New Solid State Copper Catalysts for Organic Reactions and Polymerisations

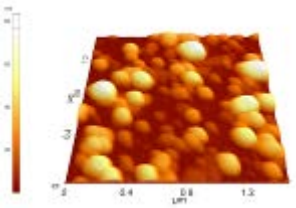


The use of a heterogeneous solid catalyst for fine chemical synthesis is thus preferable from an environmental and economical point of view. Distinct advantages of solid catalysts can include low-toxicity, ease of handling, recovery and reuse in liquid phase reactions, and the possibility of their use in a continuous process. Many heterogeneous catalysts have been previously reported in the literature to be active in organic reaction such as esterification reactions, including zeolites, titania, and acid immobilized inorganic materials. On the other hand, continuous-flow catalytic micro reactors offer safe, eco-friendly, and intensified process for the long-term production of fine chemicals. This project will develop micro reactor system using novel solid state copper catalyst for simple organic synthesis. Triazacyclononae functionalised polymers will be synthesise and their copper complexes will be grafted onto a silica or polystyrene carrier to provide a new type of solid catalyst. The catalytic performance of the solid copper catalytic micro reactor will be determined for the simple oxidation reactions such as oxidation of alkanes, benzylic oxidation, and phenol oxidation. The catalytic performance for the oxidative polymerisation will also be studied.

Discovering Bioinspired Block Co- and Terpolymers for Antibacterial Film



Bioinspired mechanisms are being used to create alternatives materials using the principles of green chemistry. Thymine, one of the nucleic bases in DNA, features both the ability to form relatively strong hydrogen bonds as well as the ability to photocrosslink. Deriving inspiration from this biological mechanism, novel water insoluble antibacterial film from poly(vinylbenzylthymine)-co- and poly(vinylbenzyltriethylammonium chloride) poly(vinylbenzylthymine)-co-poly(styrene)-co-poly(vinylbenzyltriethylammonium chloride) based on the photocrosslinking of polymeric thymines will be investigated. Polymers with quaternary ammonium groups are known to possess high anti-microbial activities. We will choose vinylbenzyltriethylammonium chloride as a monomer for one polymer block in co- and terpolymers to add anti-microbial property to the polymers.



In this project, the amphiphilic block terpolymers were synthesized by 2,2-tetramethylpiperidin-1-oxyl (TEMPO)-mediated living radical polymerization in various solution to create antibacterial film. The photocrosslinking of thymine inside the polymer film will be used to control the solubility of the polymer. The polymer morphology of synthesized polymers will also be studied. This project will involve aspect of polymer synthesis and material characterization techniques.

2. G. Kaur, S. L. Y. Chang, T. D. M. Bell, M. T. W. Hearn, K. Saito, *Journal of Polymer Science Part A: Polymer Chemistry*, **2011**, *49*, 4121–4128.

Professor Leone Spiccia

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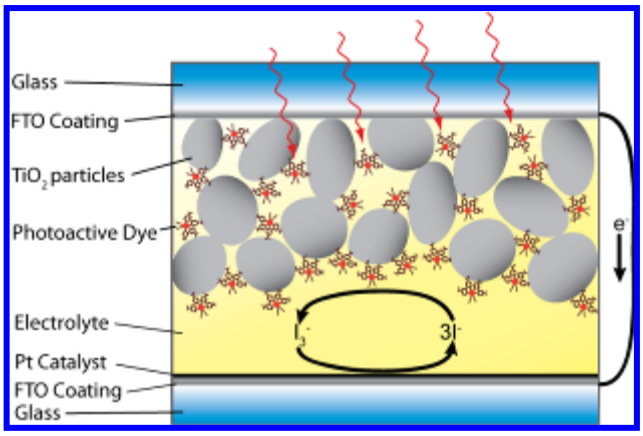
Renewable Energy Projects

Growing concerns about the impact of climate change and the diminishing reserves of some fossil fuels are driving the push for alternative, renewable energy sources that will meet the energy demands of the future. By 2050, a doubling in energy production needs to be achieved concurrently with a major reduction in greenhouse gas emissions. Many governments are setting renewable energy targets as well as legislating significant emission reductions and introducing measures such as carbon pricing. The Honours Projects described below focus on the conversion of solar energy into either electricity (dye sensitized solar cells) or fuels (solar hydrogen).

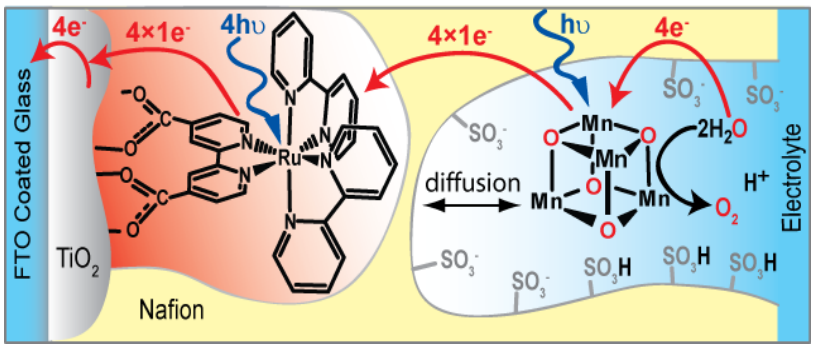
Dye sensitised solar cells (DSSCs)

DSSCs are viable alternatives to 'classical' photovoltaics. As shown in the Figure, they typically consist of a nanostructured titania film coated with a monolayer of photoactive dye (often a Ru(II) complex) and an electrolyte containing a redox couple (normally iodide/triodide, I_3^-/I^-). We are developing new non-volatile redox couples in an effort to improve the efficiency and long-term stability of DSSCs. We recently discovered that the very well known ferrocene redox couple can be used to replace the very corrosive I_3^-/I^- redox couple (Daeneke et al., *Nature Chem.*, **2011**, *3*, 211). We also shown that water can be used to replace the organic solvents commonly used in the electrolytes (Daeneke et al., Adv Mater., **2012**, *24*, 1222). In an Honours project, we would like to develop new ionic liquid, plastic crystal and/or water based electrolytes for DSSCs which incorporate the less corrosive ferrocene redox couples and a variety of transition metal complexes.



Solar Hydrogen

Hydrogen is considered the ideal clean fuel for the future and achieving the "Hydrogen Economy" is a goal of many nations. When burned in fuel cells in the presence of oxygen, it produces water as the only waste product. Ideally hydrogen would be produced from the splitting of water but this is energy intensive and expensive (typically achieved by electrolysis, which produces hydrogen at the cathode and oxygen at the anode). Using sunlight to split water is an ideal approach to a renewable source of hydrogen. To date, however, this development has been hampered by the lack of efficient photo-catalysts. In nature, the ***only*** natural catalyst to sustain water oxidation is a tetranuclear Mn-cluster, often referred to the Water Oxidation Centre, which is found in ***all*** photosynthetic organisms. Using this natural catalyst as inspiration, we recently developed a polymer membrane doped with a Mn-cluster that catalyses water oxidation for several days (*Angew Chem., Int. Ed.* 2008, **47**, 7335). We have combined this catalyst with light absorbing



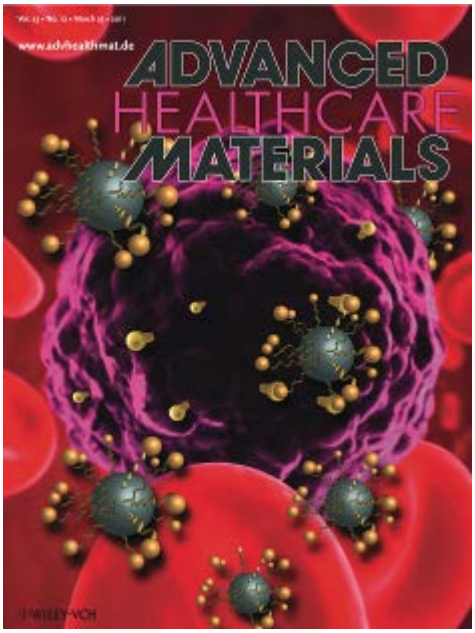
antennae (Ru(II) dyes) to create a photoanode (see Figure) which like plants uses only sunlight as energy input to oxidize water (*J. Am. Chem. Soc.*, **2010**, *132*, 2892).

Detailed EXAFS/XANES and electron microscopy experiments have revealed that a manganese mineral, called birnessite, can be generated within the Nafion films, which catalyses water oxidation. In nature, this mineral is made by bacteria and its photoactivity is responsible for the high levels of Mn^{2+} in the upper oceans (Hocking, et al., *Nature Chem.*, **2011**, *3*, 461). Honours projects are available which seek to exploit these findings by exploring new catalysts and creating nanostructured architectures with better solar energy conversion efficiencies.

New Agents for the treatment of HIV (with Assoc. Prof. Lisa Martin and Dr Bim Graham, Pharmaceutical Sciences)

The development of anti-HIV drugs continues to be a major area of research. A key step in HIV replication is adduct formation between an mRNA sequence called the "trans-activation response" (TAR) element and a "Tat" protein. There is much interest in agents that inhibit viral replication by binding to the TAR element. In studies of the effect of aminoglycoside antibiotics on HIV-mRNA, we discovered that these molecules not only bind to mRNA, they also cleave it (hydrolyse). This also occurs to other RNA targets, such as the bacterial ribosomal RNA (rRNA), which have sites that bind the aminoglycoside (see *Org. Biomol. Chem.*, **2009**, *7*, 30). Our finding paves the way to the development of potent agents that catalyse RNA cleavage rather than inhibiting replication through simple binding. Once the target is destroyed, the agent can be released to carry out further reactions. We have also shown that aminoglycosides in combination with metal complexes lead to site-specific cleavage of the target RNA (see *J. Am. Chem. Soc.*, **2009**, *131*, 1106). One issue impacting on the application of these conjugates is the ability to pass through cell where they can act on the target biomolecule. Assoc. Prof. Martin and her group have developed techniques that allow *in vitro* measurements membrane permeability of these molecules (Piantavigna, et al., *BBA - Biomembranes*, **2011**, *1808*, 1811). A project is available which seeks to develop modified aminoglycoside antibiotics, based on neomycin B, and to examine the ability of these derivatives to penetrate through biological membranes.

Cancer imaging and therapeutic agents (with Drs Bim Graham and Holger Stephan (Hemlholtz Zentrum Dresden).



The assembly of nanomaterials which combine photoactive molecules with radioactive metal complexes and MRI contrast agents offers tremendous opportunities for the developing of effective medical diagnostics and therapeutic agents (see Barreto, et al., *Adv. Mater.*, **2011**, *23*, H18-H40). We are interested in applying functionalised nanoparticles in the imaging of cancer via a combination of positron emission tomography (PET), magnetic resonance imaging (MRI) and fluorescence imaging. The aim of this project is to prepare magnetic iron oxide nanoparticles of controlled size and shape and to then decorate them with molecules that facilitate their entry through the porous vascular structure of cancer cells, and with macrocyclic ligands that allow for the introduction of a radioisotope (e.g., $^{64}Cu/^{67}Cu$) and photoactive ruthenium complexes.

Dr Andreas Stasch

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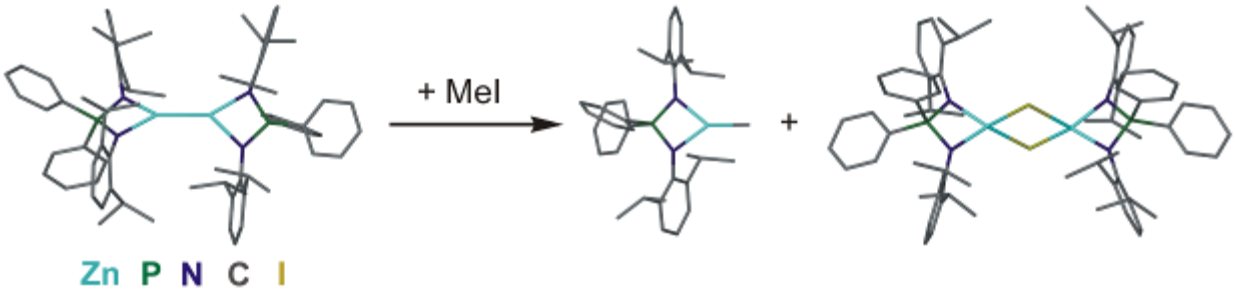
These research topics in inorganic and organometallic chemistry focus on molecules with elements in novel unusual bonding modes and rare oxidation states. They generally show novel structures, have unseen properties and as a consequence often show a unique reactivity that can be exploited for new chemistry.

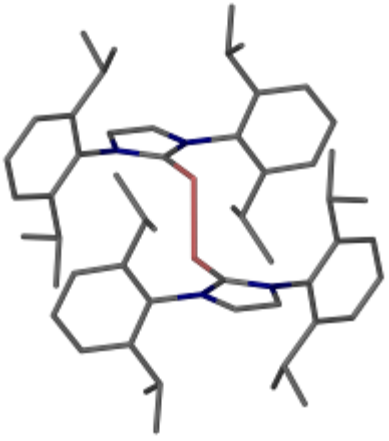
Unusual complexes of sterically demanding diiminophosphinate ligands

The development of new ligands and investigation of their further chemistry to access novel and unusual inorganic and organometallic complexes plays a pivotal role in discovering new functionalities and transformations. Very recently, we have prepared a diiminophosphinate ligand that typically forms very stable and sterically demanding complexes. The complexes (*e.g.* see picture) are typically well crystallizing and generally allow easy separation and structural characterization. The central phosphorus atom enables facile reaction monitoring by NMR spectroscopy. Your aim will be to develop the new chemistry of this ligand and related species with a range of main group elements. The project includes the preparation and characterization of new compounds with elements in unusual oxidation states and rare coordination geometries and to investigate their further reactivity. The example shows a crystal structure of a dimeric zinc(I) compound (left) and its reactivity with small alkyl halides.



For a general review on PN systems see: A. Steiner, S. Zacchini, P.I. Richards, *Coord. Chem. Rev.* **2002**, *227*, 193. The zinc(I) system: A. Stasch, *Chem. Eur. J.* **2012**, in press.

Dimeric magnesium(I) compounds as selective reducing agents in inorganic and organometallic chemistry (with Prof. C. Jones)

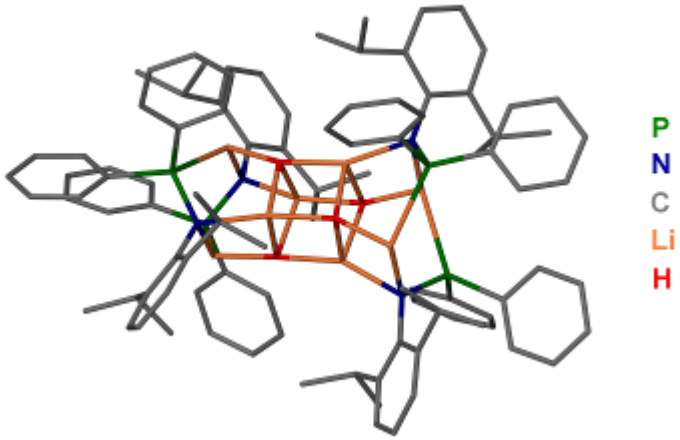


Recently we have prepared the first stable magnesium(I) compounds with the general formula LMgMgL (L = monoanionic ligand).[1] These easy to synthesize, 'bottleable' and hydrocarbon soluble reduced magnesium complexes can act as very selective reductants for organic substrates.[1] In addition, we have found that they also possess invaluable properties as highly selective reducing agents in inorganic and organometallic chemistry that generate novel reduced metal complexes.[1] These are typically not accessible using 'classical' reducing agents such as Na, K, KC_8 etc. Especially promising have been reductions of simple N-heterocyclic carbene (NHC) stabilized adducts of various element fragments leading to very unusual new donor stabilized small molecules such as Al_2H_4 [2] and Ge_2 (see picture, Ge: red, N, blue, C, grey).[3] Your

project will include the preparation of new and known metal complexes using common NHC and phosphine donor ligands and investigate their reductions using magnesium(I) compounds. See: 1: A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40*, 5659 (a review); 2: S.J. Bonhady *et al.*, *Nature Chem.* **2010**, *2*, 865; 3: A. Sidiropoulos *et al.*, *Angew. Chem. Int. Ed.* **2009**, *48*, 9701.

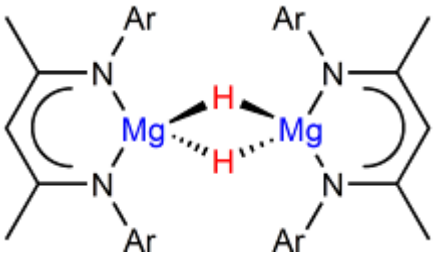
Synthesis, structure and reactivity of molecular group 1 metal hydride complexes

The 'saline' hydrides of the alkali metals, LiH, NaH, KH etc, are widely used laboratory reagents, but they are insoluble in common solvents due to their high lattice energies and as a consequence have a relatively low reactivity. Also, these fundamental light metal hydrides are of interest due to their high hydrogen content for hydrogen storage technologies. Very recently, we have presented a convenient and facile synthesis of a hydrocarbon-soluble lithium hydride complex (see picture) prepared from an alkyl lithium complex and a silane. The central $(LiH)_4$ cube in its centre resembles the bulk phase of LiH as determined by an X-ray crystal structural analysis. The $Li_8H_4^{4+}$ metal hydride core is protected by four sterically demanding phosphinoamide ligands developed by us. The presented LiH complex has been shown to cleanly and rapidly undergo a hydrolithiation reaction with benzophenone in good yield. The goal of this project is to stabilize new types of soluble group 1 metal hydride complexes, with the possible extension to yet unknown molecular NaH and KH complexes, and introduce these as reagents to synthesis. You will use a range of neutral and anionic N-ligands to assemble small and large metal hydride complexes and investigate their properties. See: A. Stasch, *Angew. Chem. Int. Ed.* **2012**, *51*, 1930.



Synthesis, structure and reactivity of molecular group 2 metal hydride complexes
(with Prof. C. Jones)

Rare hydride complexes of the group 2 metals (*e.g.* Mg, Ca) have only recently been accessible as well-defined molecular compounds in good yield. We developed a route to a β-diketiminate magnesium hydride complex (see picture; Ar = aryl group) that is thermally very stable and shows a unique reactivity. These complexes undergo unique and selective hydrometallation reductions of unsaturated organic substrates that for comparison do not react with the respective bulk metal hydrides (*e.g.* MgH_2, CaH_2). Also, these sought after complexes are of considerable interest for hydrogen storage technologies. Your project will involve the development of new metal hydride complexes using neutral and anionic ligands and investigate their further reactivity and potential use for hydrogen storage technologies. See for example: S.P. Green, C. Jones, A. Stasch, *Angew. Chem. Int. Ed.* **2008**, *47*, 9079; J. Spielmann, S. Harder, *Chem. Eur. J.* **2007**, *13*, 8928; M. Arrowsmith, *et al.*, *Angew. Chem. Int. Ed.* **2009**, *48*, 4013; S.J. Bonyhady *et al.*, *Chem. Eur. J.* **2010**, *16*, 938.



Dr Rico Tabor

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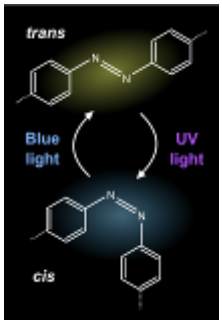
Our group is exploring a wide range of soft materials and self-assembled systems, for novel liquid crystals, advanced pharmaceuticals and technology applications. Themes range from synthesis and analysis to formulation and instrumental design. Some of our current interests are detailed below; projects are available to pursue these topics, and others.

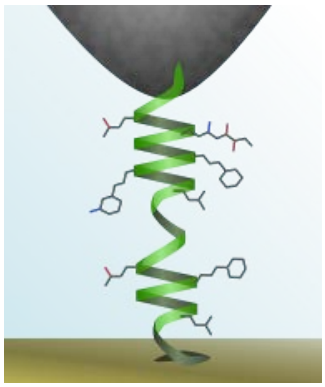
More information on our research can be seen at: ***www.ricotabor.com***

Light-switchable surfactants for smart liquid crystals

Surfactants are amphiphilic molecules – that is, they have one end that is water-loving, and one end that is water-hating. These dual characteristics give them an astonishing variety of properties connected with their self-assembly, ranging from the formation of liquid crystals and micelles to the membranes of biological cells. By incorporating a light-sensitive group into surfactant molecules, we have developed systems whose properties can be reversibly switched using UV or visible radiation. At the flick of a switch, a liquid crystal phase can be changed, an emulsion can be destabilized, or a chemical payload can be delivered.



In this project, you will explore the properties a range of new photo-active molecules based on the azobenzene group (some already synthesized, and some which you will make), including their surface activity, formation of liquid crystals and solution chemistry. Their photo-switching properties are of particular interest, and preliminary experiments have demonstrated larger-than-expected changes in system properties. The atomic force microscope (AFM) will be employed to uncover the morphology of self-assembled phases and understand photo-switching *in situ*.



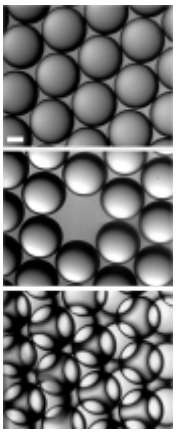
Nano-mechanics of proteins (with Assoc. Prof. Lisa Martin)

The function of proteins and other biomolecules is intrinsically linked to their conformation – hydrogen bonds and the hydrophobic interaction favour specific coiling and assembly of molecules, allowing them to orient and function within membranes, organelles and tissues. Using the atomic force microscope (AFM), you will probe the mechanical properties of proteins one molecule at a time, at the nano-scale. We seek to uncover information on their structure, and why and how they locate in the lipid bilayers that form cell membranes.

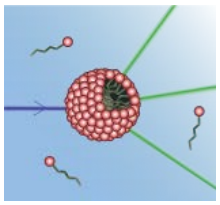
You will work with a crucial class of protein communicators – the cytochrome P450s. With the AFM cantilever, you will capture single protein molecules, explore their specific interactions with lipid environments and watch them unfold to understand their mechanics. Using complementary techniques such as the quartz crystal microbalance, you will form a full picture of how these molecules orient and function in biological environments.

Novel fluorocarbon materials for drug delivery and stabilisation

One of the most persistent and limiting problems in the treatment of diseases such as cancer is that the most aggressive, and hence effective drugs are (by their nature) also the most toxic to the healthy tissues of the body. This leads to unpleasant side effects, and limits the doses that can be administered. Approaches to overcome this issue include designed drugs with greater cell-selectivity once in the body, formulations to achieve targeted delivery or sustained release (slowing the release of the drug once inside the body). You will develop soft matter phases that will provide a system with two key attributes: a hydrophobic environment in which to dissolve hard-to-administer drugs, and an internal structure that slows release. A unique and novel aspect is that these phases will be based on fluorinated molecules that self-assemble into structured phases. Because fluorocarbons mix with neither oils nor water, the persistence of such structures should be much greater than the hydrocarbon analogues currently used.



This project will concentrate on the formulation and structural analysis of new phases. Once promising candidates have been identified, you will determine their properties for the solubilisation and release of drug molecules. These studies will be backed up by more advanced microscopy and microfluidic analyses, to understand the persistence lifetime and delivery capacity of the phases you discover.

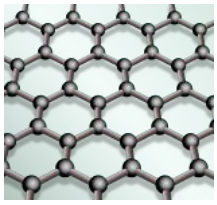


Self-assembling fluorophores: undercover chemistry (with Dr Toby Bell)

Molecules that fluoresce have revolutionized the visualization of biological samples, acting as probes and tags for specific structures and organelles within cells and tissues. Fluorescence has also become a powerful method for understanding solvation, assembly, polarity and other properties of molecules *in situ*. Your task will be to analyse the fluorescence and aggregation properties of a pair of newly synthesised molecules that appear to be particularly sensitive to their solvent environment. You will use fluorimetry, fluorescence microscopy, tensiometry, UV-vis spectroscopy and more to catalogue their properties and assess their effectiveness as environmentally-sensitive probes in solvent and biological systems.

Based on your results, we will design structural improvements to the molecules, and you will be able to synthesise new, upgraded versions. You will find new ways to deploy these labels in biological and colloidal systems, probing fundamental interfacial processes. One challenge is to design the fluorescent label such that it can ‘spy on’ biological molecules such as proteins, reporting back on their shape, function and environment.

Interfacial processing and properties of graphene



Few materials have generated as much interest as graphene – single sheets of carbon atoms with remarkable electronic and mechanical properties. We are interested in how graphene behaves at air-liquid and liquid-liquid interfaces, as this may provide new methods for processing and functionalising it, as well as suggesting a range of new composite phases with exciting properties.

Working with both pure and functionalised graphene that you synthesise, you will use a combination of analytical techniques including atomic force microscopy and novel optical methods to understand how to trap graphene at fluid interfaces, and its properties once there. You will assess its capabilities as a stabiliser, and seek new methods to change its properties *in situ* at interfaces. The end goal is to make new soft materials that combine the desirable properties of fluid phases with the strength and electronic capabilities of graphene.

Dr Kellie Tuck

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This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me (details above).

More information on my research can be seen at: ***www.chem.monash.edu.au/staff/tuck.html***

Alternate Assay Methods for Pantothenate Synthetase

Pantothenate (otherwise known as Vitamin B_5) is involved in essential biosynthetic pathways. Inhibition of its biosynthesis represents an exciting target for the development of novel antibiotics. The current assay for pantothenate synthetase is a coupled assay which uses three coupling enzymes. A more efficient assay would be the use of a fluorescent probe (chemosensor, Fig. 2) to detect the presence of an enzymatic product.

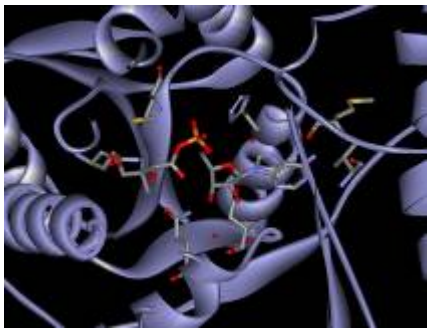

Figure 1 Image of the active site of pantothenate synthetase

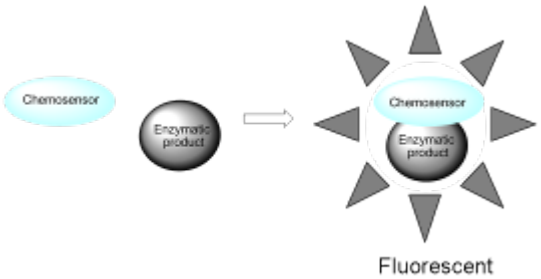

Figure 2 Action of the fluorescent probe

This project will investigate a completely new approach to monitoring the activity of ATP utilizing enzymes, we will address the problems associated with the current assay method, and devise a chemosensor that will be more amenable to the high-throughput screening of potential enzyme inhibitors.

Peptide Mimics with Potential Non-addictive Analgesic Properties.

with Dr Peter Duggan (CSIRO*)*

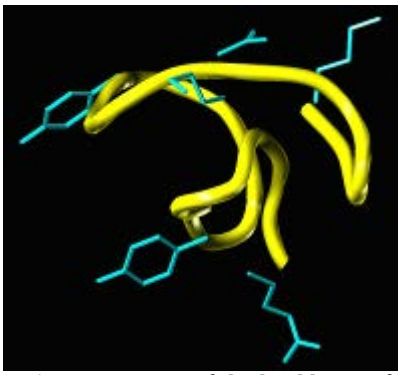

Figure 3 Image of the backbone of ω-conotoxin GVIA (yellow) with main amino acid side chains thought to be responsible for activity (teal)

This project involves further development of peptide mimics inspired by the cone shell toxin, ω-conotoxin GVIA (Fig. 3), a small cystine knot which binds tightly to neuronal N-type calcium channels. GVIA has non-addictive analgesic properties but is not suitable for use as a drug because of its very strong binding to the calcium channel. In addition, it suffers from the usual unfavorable characteristics associated with peptides such as low bio-availability. Peptide mimics have been designed with the aid of molecular modeling and aim to simulate the way key amino acid side chains of GVIA are presented to the receptor. First and second generation compounds have been tested and show very promising activity. We are now involved in investigating benzimidazole mimetics to improve activity.

Honours projects in this area will involve the synthesis of analogues of active compounds and to probe their binding modes to *N*-type calcium channels. Analogues prepared by honours students will be tested for biological activity.

For useful background information see: ω-Conotoxin GVIA mimetics based on an anthranilamide core: Effect of variation in ammonium side chain lengths and incorporation of fluorine. Andersson, A., Baell, J. B., Duggan, P. J., Graham, J. E., Lewis, R. J., Lumsden, N. G., Tranberg, C. E., Tuck, K. L., Yang, A. *Bioorg. Med. Chem.* **2009**, *17*, 6659–6670.

BCL-X_L antagonists based on α-helix mimicry for cancer therapy.

with Dr Peter Duggan and Dr Adam Meyer (CSIRO), collaboration with Dr Guillaume Lessene (WEHI)

$BCL\text{-}X_L$ is pro-survival protein overexpressed in many types of cancer, and it protects transformed cells from apoptosis. Natural pro-apoptotic proteins interact with BCL-XL via an α-helical peptide sequence known as the BH3 domain to trigger an apoptotic cascade, leading to cell death. We have developed facile modular synthetic approaches to pyrimidine-based scaffolds such as the phenyl-pyrimidine-oxadiazole 1 (Fig. 4b), and established that this particular scaffold has an appropriate spatial arrangement of substituents to mimic the i, i+3 and i+7 positions of an α-helix (Fig. 4c). This honours project will involve the synthesis of novel scaffolds with the key amino acid residues to mimic the BH3 domain of appropriate pro-apoptotic proteins. This strategy therefore holds great promise as a means of enabling the discovery of new non-peptidic BCL-XL antagonists as potential cancer therapeutics.

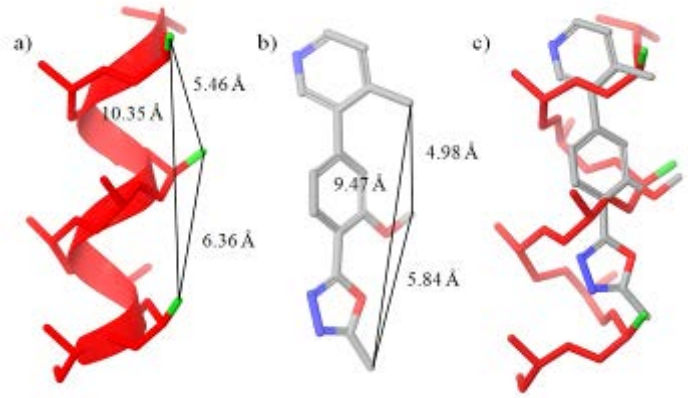

Figure 4: a) polyalanine α-helix showing *i*, *i*+3 and *i*+7 R-group distances; b) energetically minimised triaryl scaffold showing R-group distances; c) minimised triaryl scaffold overlayed onto a polyalanine α-helix.

A chemosensor for heavy metals at environmentally relevant concentrations.

with Assoc. Prof. Mike Grace

High concentrations of Zn^{2+} can cause severe environmental problems in our waterways. Quantification of the cation concentration rather than the total concentration of zinc, by conventional means, is very difficult and tedious. Recently we have discovered novel, fluorescence based chemosensors to selectively detect environmentally relevant concentrations of Zn^{2+} (*Tetrahedron Letters*, **2010**, *51*, 1161–1165 and Fig. 5). These sensors show high selectivity for Zn^{2+} over other cations, and are functional at environmentally relevant pH with detection limits of 0.05 μM for free Zn^{2+}. This project will explore this exciting new class of fluorescent probes by synthesizing the existing probe and new target fluorescent probes. The probes will then be used to determine the level of toxic Zn^{2+} in several Melbourne wetlands.

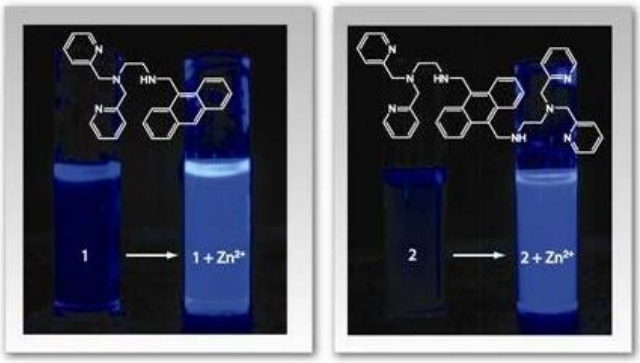

Figure 5 Chemosensors in the absence and presence of Zn^{2+}; illuminated with a hand-held UV lamp.

Dr David Turner

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This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me (details above).

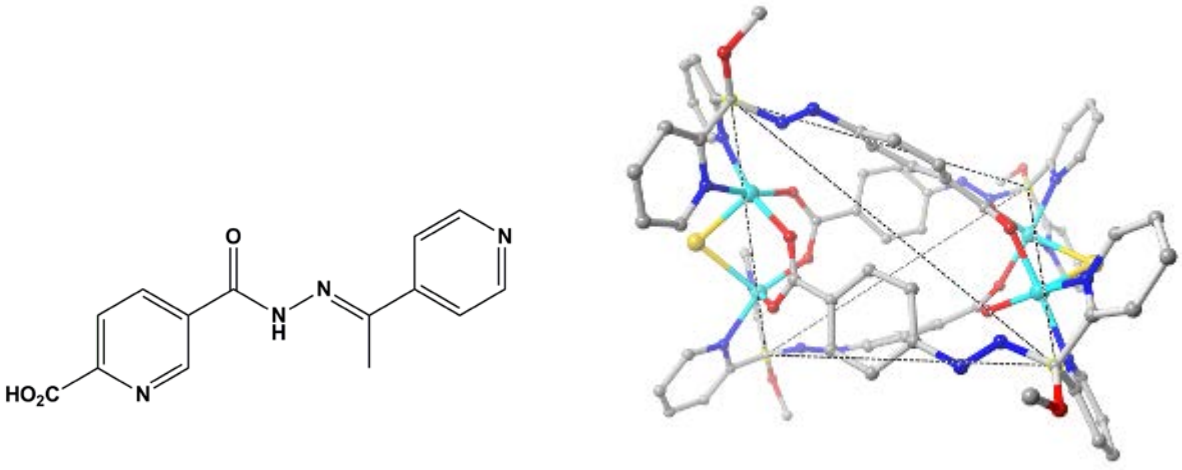
More information on my research can be seen at: ***www.chem.monash.edu.au/staff/turner.html***

Metal-Organic Frameworks and Polyhedra

The formation of either polymeric materials or discrete complexes that comprise a framework of metal ions connected by organic bridges is highly topical. A notable emphasis of this research is an attempt to control the topology or shape of the framework in a predictable manner with the aim of creating porous or hollow materials/polyhedral.

This project will examine a series of organic bridges, or ligands, that contain functional groups that are potentially able to form hydrogen bonds with anions in addition to their coordinating ability. By using ligands that associate strongly with the anions we can attempt to assemble networks by using the anions as templates around which the ligands gather. In this manner we can alter the topology of our coordination networks by changing which anion we use during the synthetic procedure. This project will utilize a variety of non-symmetric ligands that incorporate a hydrogen-bonding hydrazinyl unit between the coordinating ends. Reactions with metals occur under self-assembly conditions which frequently yield fascinating – if sometimes unpredictable – structures, whose properties will be explored.

The project will involve synthesis of both the organic ligands and their metal-complexes and structural analysis by diffraction, primarily using the Australian Synchrotron. We have recently made a novel Cu-tetrahedron (see below) and a plethora of coordination polymers – your contribution is waiting to happen!



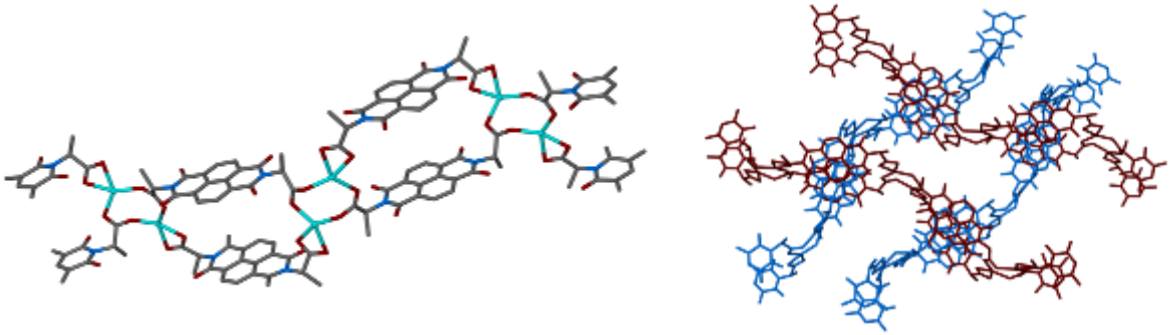
An example of a target ligand and a previously synthesised metal-organic tetrahedron using a similar organic bridge.

Chiral Framework Materials for Separation

Coordination polymers, or 'metal-organic frameworks', are materials in which organic molecules bridge between metal-ions to form a 3D network. This project will use amino-acid-based ligands that have the potential to form materials that contain empty, chiral channels. The target materials are porous frameworks in which solvents, gases or other small organic molecules can be placed with a particular emphasis on separation of enantiomers, by selective adsorption, or strong and reversible binding of gaseous guests. It is anticipated that the fluorescence behavior of the material will be dependent on the guests that are held within the lattice thereby the material will act as a sensor.

A series of ligands will be synthesised that are based on a naphthalene diimide (NDI) core. By varying the nature of the coordinating group we can vary the topology and properties of the resulting coordination

polymers. The project will involve the organic synthesis of the ligands, synthesis and structural studies of coordination polymers (typically involving the Australian Synchrotron) and investigations into their guest storage properties (in collaboration with CSIRO). Our previous results are very promising (see below) and there is massive scope to create your own array of new, porous materials.

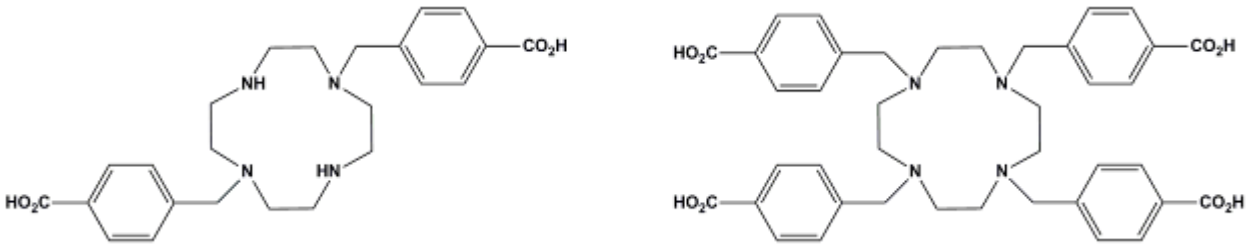


An Mn-based network containing NDI ligands (left) which form an interpenetrated structure with potentially guest-accessible, chiral channels (right).

Amine-Based Porous Materials for CO_2 Capture (with Prof. Stuart Batten)

This project forms part of a multi-institution, multi-disciplinary effort to synthesise and study porous metal-organic materials that are capable of strong and selective CO_2 gas uptake. Traditional solution-phase methods for CO_2 scrubbing rely on aqueous amine solutions. The aim of this project is to incorporate free amines into framework materials that can provide strong, selective and reversible binding of CO_2.

This project will attempt to incorporate amine-containing macrocycles into coordination polymers (porous frameworks constructed using metal ions and organic bridging ligands). You will be using a wide range of different macrocycles and coordinating groups with a 'modular' approach to ligand construction. The project will involve the synthesis of both the organic ligands and the final materials, structural analysis of the materials (using the Australian synchrotron) and, hopefully, analysis of the gas storage properties of the wonderfully porous materials that you make!



Examples of the types of ligands that will be targeted during this project. The size and substitution of the macrocycle and the types of coordinating groups will be varied.

Dr Brendan Wilkinson

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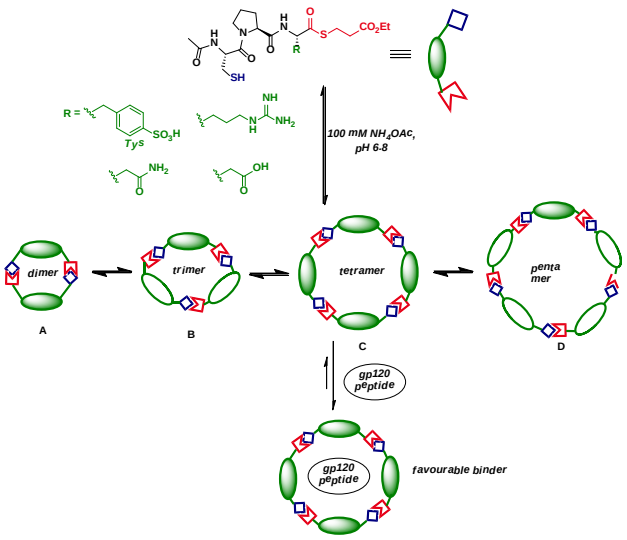
Our group is interested in exploring dynamic combinatorial chemistry (DCC) as a synthetic tool for probing carbohydrate-protein and protein-protein interactions, with particular emphasis on the discovery of new drug leads for the treatment of cancer, viral infection and autoimmune diseases. The following projects will give you an idea of the type of research we are undertaking within my group. If you have any further questions, do not hesitate to contact me (details above).

Dynamic cyclic sulfopeptides as inhibitors of HIV entry



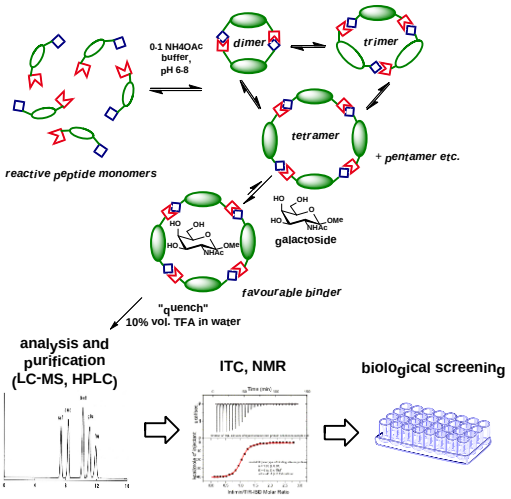
The entry of human immunodeficiency virus-1 (HIV-1) into the host cell is mediated by the binding of gp120 envelop glycoprotein to host receptors CD4 and CCR5. This essential binding event requires high-affinity electrostatic interactions between *O*-sulfated tyrosine residues (Tys) within the N-terminal region of CCR5 and positively charged residues in the gp120-CD4 binding pocket.[1] Cyclic peptidomimetics of CCR5 are promising drug leads as HIV entry inhibitors.[2] This project will employ DCC as a tool for the synthesis and high throughput screening of cyclic sulfopeptide libraries as HIV-1 entry inhibitors. A panel of tripeptide thioester monomers will undergo thiol-thioester exchange in the presence of short peptide fragments of the gp120 binding pocket. Strong binders from the dynamic combinatorial library (DCL), or "hits", will be amplified and detected by analytical HPLC and LC-MS. During the course of this project, the student will develop a broad range of skills ranging from organic synthesis, analytical HPLC and LC-MS, molecular modeling, isothermal titration calorimetry (ICT) and NMR.

References

[1]. Huang,C, C.; Lam, S. N.; Acharya, P.; Tang, M.; Xiang, S. –H.; Hussan, S. S.; Stanfield, R. L.; Robinson, J.; Sodroski, J.; Wilson, I. A.; Wyatt, R.; Bewley, C. A.; Kwong, P. D. *Science*, **2007**, *317*, 1930-1934.

[2]. Seitz, M.; Rusert, P.; Moehle, K.; Trkola, A.; Robinson, A. *Chem. Commun.* **2010**, **46**, 7754–7756.

Synthesis and screening of biomimetic carbohydrate receptors using dynamic combinatorial chemistry (DCC)



The Galectins are an ancient family of β-D-galactoside binding proteins found in virtually all living organisms. They regulate a wide range of important physiological and pathophysiological processes including immune regulation and inflammation, cellular development and apoptosis, and cancer.[1] Galectin-1 (Gal-1) and Galectin-3 (Gal-3) are over-expressed in many tumour tissues, such as melanomas, astrocytomas, bladder and ovarian tumors and are correlated with tumour angiogenesis and metastasis.[2] This project will employ DCC to synthesize and screen a library of dynamic cyclic peptides as synthetic carbohydrate receptors mimicking the Gal-1 and Gal-3 carbohydrate recognition domain. The DCLs will be prepared and screened using reversible chemical processes (e.g thiol-disulfide exchange) in the presence of a β-galactoside ligand. Favourable binding interactions will result in amplification of the DCL as determined by analytical HPLC and LC-MS. Gal-1 and Gal-3 inhibitors synthesized in this project will represent promising drug leads for the treatment of a variety of cancers.

References

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2. Thijssen, V. L; Poirier, F.; Baum, L. G.; Griffioen, A. W. *Blood* **2007**, *110*, 2819–2827.

Self-assembled cyclodextrin mimics for drug delivery.

Cyclodextrins (CD) are cyclic oligosaccharides possessing a hydrophilic outer surface and a hydrophobic inner cavity. The unique physicochemical properties and three-dimensional shape enable CDs to form inclusion complexes with poorly soluble molecules in aqueous solvents.[1] As such, they are widely used as solubilizing agents and as vehicles for drug delivery.[1,2] Starting from functionalized monosaccharide monomers, we are interested in using DCC as a tool for preparing virtual libraries of CD mimics which self-assemble in the presence of added drug molecules. The adaptive behaviour of such systems provides an ideal way for studying host-guest complexes of CD mimics with various hydrophobic molecules. This project will aim to produce “designer” CDs as innovative materials with applications in the pharmaceutical, agrochemical and food industry.

References

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2. Loftsson, T.; Brewster M. E. *J. Pharm. Sci*, **1996**, *85*, 10,1017-1025.

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Diagnosing malaria at the single cell level using state-of-the art FTIR imaging, Raman confocal spectroscopy and synchrotron infrared spectroscopy

Malaria afflicts between 300-500 million people a year with a mortality that approaches 1 million per annum. Most deaths occur in children under 5 and child mortality from cerebral malaria is 20%. Of the children that survive 10 % are affected with severe neurological disorders. Strategies to diagnose malaria are based on detecting the parasite in the bloodstream. The standard technique for malaria diagnosis is bright-field microscopy. The technique has a number of advantages with the main one being the ability to quantify and identify the parasites at different stages of the parasite's life cycle. However, the technique is subjective and requires experienced personnel to make the diagnosis. Rapid diagnostic tests (RDTs), also known as 'dipsticks', make use of a capture antibody and conjugated detection antibody to detect malarial antigen in blood samples. RDTs have a rapid turnaround time and are simple to use, enabling clinicians to make on-the-spot diagnoses but the technique is not quantitative. Optical spectroscopy techniques offer a number of advantages compared to these more traditional techniques. These include non-subjective diagnosis based on using machine based recognition techniques, a minimal amount of sample required, minimizing harm to the patient and the fact that sample preparation is straight-forward. We have pioneered a number of innovative methods to diagnose malaria using Raman and infrared-based techniques. While these techniques have demonstrated the potential of optical diagnostics more innovation is required to take the technology to a clinical setting. Hitherto both Raman and FTIR spectroscopy have been applied to investigate mainly parasites at the late stage of the erythrocytic cycle known as the trophozoite phase. Figure 1A shows the type of image that can be achieved using Raman imaging while Figure B shows an FTIR image recorded of a group of infected cells using the FTIR beamline at the IRENI synchrotron in Wisconsin (USA).

The project will apply FTIR focal plane array imaging and Raman spectroscopic imaging spectroscopy in combination with a range of machine based pattern recognition systems to unequivocally diagnose malaria at all stages of the parasites life cycle in rapid time with minimal sample preparation at low cost using a bench top IR instrument.

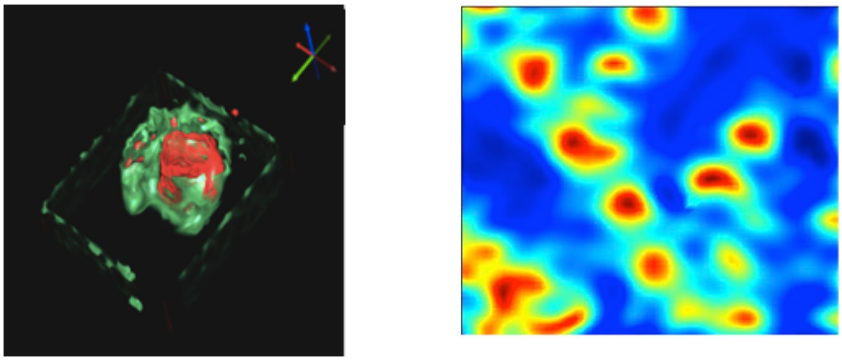

Figure 1A 3D Raman image of a malaria parasite within a red blood cell. **1B** An FTIR image of a group of infected parasites.

References

1. Webster, G. T. et al. *Analytical Chemistry* **2009**, *81*, 2516.
2. Wood, B. R. et al. *Analyst* **2009**, *134*, 1119
3. Wood, B. R.; McNaughton, D. *Expert Review of Proteomics* **2006**, *3*, 525
4. Wood, B. R. et al. *FEBS Lett* **2003**, *554*, 247

FTIR imaging spectroscopy a new approach for diagnosing canine cancer

The cancer tissue study stems from a newly formed collaboration with Dr Matti Kiupel from the prestigious College of Veterinary Medicine at Michigan State University. The project will focus on detecting new infrared biomarkers for canine cancer. This forms a part of our successful ARC Discovery project bid that commenced in 2012. We will be applying multivariate methods to two model cancers namely canine mast cell tumours and canine large-cell B-cell lymphomas, which have been previously collected and characterized by Prof. M. Kiupel, with 50% od samples deemed chemo-resistant and 50% chemo-sensitive. The advantage of a multidisciplinary collaboration such as this is that the samples will be characterized in detail by board-certified pathologists using histologic, molecular and proteomic techniques (including immunohistochemistry, DNA microarrays, immunoblotting etc.), which will then be correlated with the spectroscopic data.

Cancer grading by light microscopy is, by its nature, subjective and highly dependent on the training and experience of the pathologist examining the tissues, as well as the sample quality and quantity. Many neoplasias require ancillary diagnostics (e.g., IHC, flow cytometry, PCR) to further characterize their cell origin, clonality and / or malignant risk, and these tests are often time-consuming, laborious, costly and / or slow. Given the ease with which infrared spectroscopy can be performed on small tissue or cell samples with high precision and minimal preparation, an infrared parameter that relates to cellular biosynthetic activity may be valuable as a prognostic indicator, particularly in cases where the current "gold standards" are wanting. We will develop a multipronged approach utilizing FTIR, Raman, Fluorescence imaging and UV-Visible imaging coupled with machine based recognition systems to search for spectroscopic markers associated with neoplasia. The image data will be correlated directly with histopathological and immunochemical techniques. Using machine based recognition tools and image reconstruction techniques we will build 3D images of multiple adjacent tissue sections to investigate the shape and depth of penetration of tumours. Figure 1 shows a 3D FTIR image generated from multiple images recorded form a sample of cervical epithelium diagnosed with adenocarcinoma. The map was processed using Unsupervised Hierarchical Cluster Analysis (UHCA) which clusters spectra based on similarity. The colours represent different cell types including adenocarcinoma, red blood cells, lymphocyte exudates and connective tissue.

Figure 1 Two views of 3D cluster maps for 4 clusters obtained from analysis in the 1272-950 cm-1 spectral region. The cluster map false color scheme corresponds to brown for exudates, blue for inflamed glandular tissue, green for connective tissue and orange for blood filled capillaries as described in the text. (b). Same image made semitransparent by removing blood filled capillaries and inflamed glandular tissue.

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2. B. R. Wood et al. *Gynecologic Oncology* (93, 59-68, **2004**)

Dr Jie Zhang

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This document will give you an idea of the type of research we are undertaking within my group. If you have any further queries, please do not hesitate to contact me (details above).

More information on my research can be seen at: ***www.chem.monash.edu.au/staff/zhang***

Synthesis of new nanocomposite catalysts and their applications in green chemistry (with Mike Horne (CSIRO), Dr. Theo Rodopoulos (CSIRO), Prof. Alan Bond and Prof. Douglas MacFarlane). A scholarship of $ 5,000 will be given to the candidate with a strong academic background and research experience

Research on clean energy technologies has attracted worldwide attention due to the potential crisis in running out of conventional fuels in the foreseeable future. Electrochemistry plays an important role in the development of clean energy, the fixation of carbon dioxide (CO_2) and development of cleaner/greener and more efficient processes in all industries that manufacture or use chemicals, which are important areas in green chemistry. Research in the areas of Green Chemistry is a key strength of Monash University. The recent announcement of a $72.8 million project for the development of a Green Chemical Futures facility at the Clayton campus will strengthen Monash University's position as a key player in Green Energy production.

In this project, new multifunctional nanocatalysts will be synthesized for the electrocatalytic/ photoelectrocatalytic reduction of CO_2 in suitable reaction media at room temperature. Highly sophisticated voltammetric techniques and the corresponding quantitative theories will be developed for sample characterization and better understanding of the fundamental processes occurring at new nano-interfaces. Students will also have a chance to have hand on experience on a range of contemporary analytical Instrumentations which are available at both Monash University and CSIRO, including electron microscopes, XRD, NMR, GC-MS etc, for sample characterization/product analysis.

Fabrication of highly efficient enzyme electrodes for biosensor and biofuel cell applications (with Prof. Steven Langford and Prof. Alan Bond)

Direct electron transfer between an enzyme and an electrode is both a practical and fundamentally important problem that has attracted worldwide attention.

Due to the lack of electronic communication between a conventional unmodified solid electrode and a large enzyme, a dissolved electron transfer mediator is normally required to generate efficient enzyme electrodes. However, the presence of an electron transfer mediator is prohibitive for *in vivo* applications. In the ideal situation, direct electron transfer between an electrode and the enzyme is preferred. This is the basic concept for the third generation enzyme electrodes. However, a number of issues remain to be addressed. Enzymes are large macromolecules, and their active sites can often be buried deep within hydrophobic pockets. Moreover, once in contact with the metallic surfaces of the electrodes, enzymes are very often denatured due to a conformational alteration of their secondary structure. These issues make realization of direct electron transfer a challenge for electrochemists.

The problems inherent to direct electron transfer between an electrode and large enzymes will be addressed by using electrodes modified with electronic and ionic conducting nanocomposite materials for enzyme immobilization. As one part of the electrode, these nanocomposite materials will work effectively as electron transfer relays to promote the direct electrochemistry of the enzyme.

In this project, students are expected to carry out the following activities:

- synthesize novel nanocomposite materials
- fabricate three dimensional enzyme electrodes using nanocomposite materials to promote direct electrochemistry of enzymes with high efficiency and high stability
- understand the mechanisms of electron transfer processes involving enzymes