School of Chemistry
Honours Projects for 2014

MONASH University
Science
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**Dr. Xinyi Zhang**

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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 2014. 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 2014 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!

Assoc. Prof Mike Grace
Honours Coordinator
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Bismuth-Precursors for Antimicrobial Organic-Inorganic Hybrid Materials (with Prof. Michael Mehring at Technical Universität Chemnitz)

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 relatively non-toxic 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. 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 will investigate:

- the formation of novel bismuth(III) complexes which have high antimicrobial activity
- reproducible methods for polynuclear bismuth oxido-cluster formation and
- 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.

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-flies 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 Leishmania remain antimony (Sb) compounds; sodium stibogluconate and meglumine antimonite. These drugs are highly toxic and are given as a series of painful intra-muscular injections over 28 days. New active drugs are needed 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 antimicrobial activity of many Bi compounds means we have the possibility of synthesising new, active and safer anti-Leishmanial drugs.

In recent years we have shown that some Bi(III) and Bi(V) compounds 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 sulfonamides and oximes. 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.
Development, Efficacy and Mode of Action of New Bismuth Anti-Cancer Drugs
(with Dr Carolyn Dillon, University of Wollongong)

In contrast to other heavy metals bismuth is currently considered to have low systemic toxicity in humans. However, very little is known of its transport, storage and action in a biological environment. In vivo studies have shown that certain bismuth complexes can exert anti-tumour activity against ovarian and colon cancer. However, the anti-cancer activity of most Bi complexes has been restricted by their poor solubility properties. Recently, a new class of Bi drugs have been synthesized that exhibit greater solubility and high antimicrobial activity. To date, the anti-cancer activity of these complexes has been unexplored.

The project will initially investigate methods for the reproducible and efficient synthesis of a family of bismuth(III) compounds, establishing full structural characterization, solubility and stability. The cell uptake and anti-cancer activity of these bismuth(III) complexes will then be explored.

In collaboration with colleagues at University of Wollongong cell culture assays, including MTT and trypan blue, will be performed to investigate the anti-cancer activity of these complexes. In addition, graphite furnace atomic absorption spectroscopy and microprobe X-ray fluorescence spectroscopy will be performed to determine the uptake of the Bi complexes by breast cancer cells.

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.KOtBu]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.
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 users 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: [http://monash.edu/science/about/schools/chemistry/staff/sbatten/](http://monash.edu/science/about/schools/chemistry/staff/sbatten/)

### 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⁺, Ca²⁺, Sr²⁺, Ba²⁺, La³⁺) 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
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 CO₂, 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 H₂, CO₂, CH₄, magnetic properties, catalytic properties).

Chemistry of Small Cyano Anions (with Professor 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 Ln₁₃ 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. cmm is synthesized by addition of MeOH to dcmn), 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.
New anions from nucleophilic addition reactions

Metal clusters for Single Molecule Magnets

Coordination polymers for long-range magnetism, spin crossover, and gas sorption

Organic and lanthanoid containing ionic liquids

Crystal engineering of hydrogen bonded networks

Small Cyano Anions (SCAs)
Watching single molecules react (with Professor Steven Langford)

It is now possible to study fluorescent materials at the ultimate limit of resolution, one molecule at a time, using advanced fluorescence spectroscopic and microscopic techniques. Changes in the properties of the fluorescence from a single molecule can report on what that particular molecule is doing. This project will study single naphthalene diimide (NDI) molecules undergoing reaction with simple amines in order to reveal for the first time, what happens at the single molecule level in a substitution reaction. The reaction will be monitored by a change in colour (spectral shift) of the fluorescence when a mono-substituted NDI (yellow) reacts with amine to give the di-substituted product (red).

Sensing single protonation events by fluorescence (with Professor Steven Langford)

Fluorescence is an excellent way for sensing the presence of molecular species via a change in output of a fluorescent reporter. It is highly sensitive, minimally invasive and often species selective. It can be used to detect analytes down to ppb or even ppt levels and give a real-time read out. We want to take this sensitivity down to the ultimate level of resolution and sense protonation events occurring in single molecules. The project will utilise a recently developed a fluorescent NDI-based proton sensor which is also bright and photostable enough to see as single molecules and shows an unambiguous readout at the single molecule level.

Defocused wide field imaging of CdSe nanorods and tetrapods. (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.

Unlike spheres, rods and pods are expected to show a well-defined emission dipole. This project will make direct images of emission dipoles of single nanorods and ‘pods’ by fluorescence microscopy for the first time. It will lead to knowledge about the nature of the emission dipoles and reveal the fundamental photophysics of these important, new materials.
Super-resolution imaging of silica nano-spheres. (with Assoc. Professor Udo Bach and Dr Alison Funston)

Optical microscopy is limited by the diffraction of light so that even essentially perfect (aberration free) optics, the best resolution achievable is around 200 – 300 nm. Recently, a number of microscopy techniques have been developed which use single molecule fluorescence detection to circumvent this limit, opening up the nanometre world to fluorescence imaging. Each point in the final super resolution image is from an individually imaged molecule. Using this approach, resolutions well below 100 nm are possible. This project will assess the resolution obtainable from single molecule based super-resolution microscopy by direct comparison to electron microscopy using silica nano-spheres, 10 – 50 nm in size, coated with fluorescent dyes. Spheres of different sizes and with dyes of different wavelength will be examined.

Super-resolution imaging of chromatin. (with Dr Nico Plachta).

DNA is the molecule of life and while its alphabet is well known and has been sequenced for many species including humans, the processes by which metres of DNA are fitted into the micron sized space of a cell’s nucleus remain a mystery. At the heart of how this occurs is ‘compaction’. DNA strands coil up and around other proteins into well-ordered structures which can then pack tightly to form chromatin. Various stages of compaction are known, such as formation of nucleosomes, while others are more speculative, such as the so-called 30 nm fibre. This project will aim to use new super-resolution fluorescence microscopy techniques to image chromatin in a live cell to ‘peer in’ and reveal the various compaction and conformational states of the DNA strands and the other proteins involved in compaction.

Correlative super-resolution – atomic force imaging of lipid bi-layers. (with Dr. Rico Tabor)

Lipid bi-layers are very important self-assembled structures. They form the basis of cellular membranes and are central to the proper functioning of cells. Much material is transported across membranes both into and out of cells. A number of mechanisms contribute to this including pore formation where specific proteins and peptides, such as perforin, make holes in the lipid bilayers. These holes are very small and typically on the order of ~5 – 30 nm making them way too small to see by conventional light microscopy. This project will use both super-resolution fluorescence microscopy and atomic force microscopy to image lipid bilayers that have small pores formed in them. A range of proteins and peptides will be used and different labeling strategies and protocols developed for bi-layer imaging.
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).

**Cobalt complexes for oxygen separation**

The search is on for better ways to capture, concentrate and sequester the CO₂ 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 CO₂ and H₂O (there is no N₂ from air). Water can be easily separated by condensation, leaving the CO₂ directly available for sequestration. Commercial O₂ separation, for example by cryogenic separation, is very energy intensive - so that there is a need for a better approach. The project will focus on the development of adsorbents that could be used in a pressure swing adsorption process for O₂ separation from air. It will involve a mixture of synthetic chemistry and physical evaluation of the synthesized materials. The objective is to disperse Co organo-metallic complexes on high surface area support materials so as to achieve fast and reversible O₂ adsorption-desorption.

**Inorganic-organic hybrid materials for greenhouse gas control**  (with Professor Stuart Batten)

The project will involve a mixture of synthetic chemistry, physical evaluation and, perhaps, some computational chemistry - all focused on the development of novel metal organic framework materials (MOFs) that can be used to separate and concentrate CO₂ from major emission points (such as the flue gas from power stations). Recent work has demonstrated that very high CO₂ adsorption capacities can be achieved with some of these materials, even in the presence of moisture. The results of computational and laboratory experiments will be compared to enhance our understanding of structure-property relationships. This will potentially allow CO₂ to be captured for reuse or long-term storage (sequestration), thereby helping to minimise the Greenhouse effect.

**Turning carbon dioxide into fuel**

With the development of ‘carbon capture’ adsorbents that can concentrate large volumes of CO₂ it becomes attractive to consider the prospect for using CO₂ as a chemical feedstock. Since H₂ can be provided by solar power (e.g., photovoltaic water splitting), then this can be used to reduce CO₂ to CO or other reduced C₁ forms (e.g., formaldehyde or methanol). Methanol can be used directly as fuel in petrol engines or it can be dehydrated to dimethylether, which can be used as a diesel fuel substitute.
The project will involve the synthesis and thorough characterisation of prospective heterogeneous catalyst in which the active metal components are confined as nanoparticles within a mesoporous substrate such as SBA-15. The activity of the prepared catalysts will then be tested in a small fixed bed reactor incorporating mass spectrometry detection to determine the product distribution and reaction rates.

**Chemicals from biomass and coal (with Dr Emma Qi)**

Petroleum has been the main source of feedstocks for the chemical industry for many decades. However, as supplies dwindle and prices sky-rocket there is interest in the prospects for deriving chemical feedstocks from biomass, or from ‘low-rank’ fossil fuels which are essentially mildly degraded biomass (e.g., brown coal, oil shale). This project will determine the potential to selectively extract discrete chemical classes (e.g., phenols, carboxylic acids, aliphatic or aromatic hydrocarbons) from organic matrix (biomass or coal) and in doing so will make use of carbon dioxide, either as a supercritical fluid in its own right or as one component of novel potentially recyclable ionic liquid (e.g., DIMCARB). Extracts will be characterized by a variety of analytical techniques such as solid state NMR, GC-MS and pyrolysis-GC-MS. In addition to determining the efficiency and selectivity of the extraction methods for bulk chemical feedstocks, the project will help to delineate geochemical reaction mechanisms that occur in nature (see figure).

**Carbon dioxide utilisation**

Fuel cells can provide high efficiency power for domestic households and vehicles. Fuel cells work by allowing O\(_2\) to react with the fuel to produce electricity without combustion. In hydrogen fuel cells, water and heat are the only by-products. The required H\(_2\) can be generated by the catalytic conversion of methanol with water vapour. Typically, catalysts are of similar to those used for commercial methanol synthesis (Cu/Zn oxides on an amorphous carrier such as alumina). It is essential that the H\(_2\) is free of CO, which leads to anode degradation. The CO concentrations that can be achieved with current catalysts (ca. 0.5 to 1 vol.-% of CO) are too high.

This project will explore the potential of modified mesoporous MCM (pore diameters of 1.5-10 nm) as catalyst supports for H\(_2\) synthesis from methanol. MCM materials have been selected as carriers because they: (i) they can be synthesised in a large variety of different crystalline structures and chemical compositions, (ii) they can be modified by several techniques to tailor their surface acidity/basicity and (iii) via ion exchange or impregnation, nearly every desired catalytically active component can be introduced.
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

\[
\text{NH}_3 + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O}
\]

The reaction is mediated by the bacteria nitrosomonas and nitrobacter, which are chemoautotrophic and derive their energy from this reaction. The reaction is an essential link in the nitrogen cycle because it produces \( \text{NO}_3^- \) 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).

**The use of Biospectroscopy to quantify seagrass health** (with Assoc Professor Bayden Wood and Professor John Beardall (Biology))

Seagrass (Zostera. sp) beds form an important habitat in coastal ecosystems. There has been a dramatic decline in seagrass beds globally driven by nutrient and sediment inputs to coastal waters. Monitoring the health of seagrass is therefore of great interest to ecologists. There has recently been a great deal of focus on physiological measures of seagrass health including C:N:P ratios and isotopic approaches. All of these approaches typically use wet chemical methods which are expensive and time consuming. The aim of this project is to use spectroscopic methods to quantify seagrass health in comparison to other more commonly used approaches.
Tracing nitrogen in aquatic ecosystems using stable isotopes of nitrogen and oxygen (with Assoc Professor. Mike Grace)

Nitrogen is one of the nutrients that limits plant growth and can lead to eutrophication in aquatic ecosystems. Tracing sources of nitrogen to aquatic ecosystems is critical to efforts to reduce nitrogen loads. The stable isotopes of Oxygen ($^{18}\text{O}$) and Nitrogen ($^{15}\text{N}$) in NO$_3^-$ can be used to provide information on the sources and cycling of this plant nutrient. This project will use a newly commissioned mass spectrometer within the Water Studies Centre to undertake stable isotope measurements of NO$_3^-$ to trace its source in local waterways (fresh, estuarine and groundwater).

A new approach to measuring nitrogen fixation in seagrass beds (with Professor John Beardall (Biology))

Nitrogen is generally the nutrient that limits plant growth in the marine environment. Bacteria associated with the roots of seagrass are known to be able to convert atmospheric N$_2$ into NH$_4^+$ through the process of N$_2$ fixation. Quantifying this process is challenging because it is hard to measure small changes in nitrogen concentration against a large background and the process has a large temporal variability. The nitrogen fixation reaction has a small amount of isotopic discrimination which means that newly fixed nitrogen will have a unique $^{15}\text{N}:^{14}\text{N}$ ratio compared to nitrogen derived from already fixed sources (e.g. water column NH$_4^+$ and NO$_3^-$). This means that seagrass is generally isotopically lighter than other aquatic plants. If the $^{15}\text{N}:^{14}\text{N}$ ratios of newly fixed nitrogen and the nitrogen sources are known then the contribution of newly fixed nitrogen to plan growth can be calculated. This project will investigate the use of $^{15}\text{N}:^{14}\text{N}$ ratios in plant biomass and nutrient sources (sediment nitrogen) to measure rates of nitrogen fixation in seagrass beds.
Rare earth elements (Group 3-Sc, Y, La and the lanthanoids Ce - Lu)

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. Our group provides fundamental knowledge to underpin industrial developments in the area. 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, and catalysts for artificial rubber production. 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-NR₂) and aryloxides (Ln-OAr), and have developed unique synthetic methods to obtain them. Features of these compounds include low coordination numbers and extraordinary reactivity. To prepare and structurally characterize the compounds represents a major challenge. The program involves extensive international collaboration.

Heterobimetallic complexes (with Professor 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) 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. The studies represent a bridge between metal-organic and solid state chemistry, as such they represent a major new initiative in inorganic synthesis. Besides X-ray crystallography and powder photography, use of vacuum/N₂ 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 Professor Peter Junk (JCU))

Isolation of lanthanoid complexes in unusual oxidation states, e.g. Y²⁺ has been a frontier science development in recent years, and the first Nd²⁺ 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 Yb²⁺ and Sm²⁺ complexes is a major challenge. If it can be achieved the Ln²⁺ complexes have great potential for interesting redox chemistry.
New Approaches to Metal-Based Syntheses (with Professor Peter Junk (JCU) and Professor Phil Andrews)

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. As these have mainly used organomercurials or organothallium 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 triaryl bismuth compounds, (c) use of lanthanoid pseudo-Grignard reagents such as PhYbI, MeEuI etc. Examples of each of these exciting possibilities follow:

(a) \( \text{Ln}(I_2) + 3\text{LH} \rightarrow \text{LnL}_3 + 3/2\text{H}_2 \)

(b) \( 2\text{Ln} + 3\text{BiAr} + 6\text{LH} \rightarrow 2\text{LnL}_3 + 3\text{Bi} + 6\text{ArH} \)

(c) \( \text{PhLnI} + \text{LH} \rightarrow \text{LLnI} + \text{PhH} \)

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. Although BiPh₃ has succeeded with alkaline earth metals (*Chem. Commun.* 2008, 4490), it appears not sufficiently reactive to use with the rare earth elements, hence the more reactive Bi(C₆F₅)₃ is to be examined. This novel compound should also be a much better Lewis acid than BiPh₃ and be able to have a rich coordination chemistry.

Green Corrosion Inhibitors (with Professor Peter Junk (JCU), Dr David Turner and Professor 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. The most widely used inhibitors to combat corrosion have been based on chromates. These are now recognised as being harmful to health and the environment, and alternatives are being 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. The Figure shows visible signs of corrosion protection on a steel coupon after 7 day immersion (left) and unprotected (right) in 0.1 M NaCl with and without 500 ppm [Ce(salicylate)₃.H₂O] respectively.

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

Small cyano anions such as dicyanonitrosomethanide, \([\text{C(CN)}_2\text{NO}]^-\) (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 and 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 \([\text{Ln} (\square\text{dcnm})]_3^{3-}\) and carbanatolanthaballs as illustrated by the beautiful Gd₁₄ Gadoball.
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/funston

Metal Nanoparticles and Nanowires as Nanoscale Optical Fibres

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 gold and silver nanoparticles and nanowires and the testing of the ability of these structures to transmit light from one end of the structure to the other. A number of projects are available in this area.

### Changing the Colour of Nanoparticles: Nanoparticle Coupling

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 colloidal 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, 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.

Fluorescent Polymer:Nanocrystal Hybrids for Solar Photovoltaics
Semiconductor nanocrystals, such as CdSe quantum dots (QDs), are highly fluorescent. The fluorescence wavelength may be modified by changing either the size of the QD. Conjugated polymers are also highly fluorescent. This project will involve the synthesis and characterisation of CdSe nanoparticle-conjugated polymer hybrids, including their fluorescence properties. The hybrids will take advantage of the high absorption cross-section of the QD and the charge-transporting properties of the conjugated polymers and have potential use in solar energy conversion. The project will make use of absorption and fluorescence spectroscopy (steady-state and time-resolved), transmission electron microscopy (TEM) and atomic force microscopy.
Associate Professor Mike Grace
Room No. G25c, Tel: 9905 4078, email: michael.grace@monash.edu

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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.
Contructed wetlands – environmental benefactors or villains?

This project will examine the extent to which wetlands around Melbourne generate greenhouse gases (GHGs) including CH₄, N₂O and CO₂. 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 P 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 ¹⁵NO₃⁻ (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 N₂ gas but may also be converted to the potent greenhouse gas, N₂O, or reduced to ¹⁵NH₄⁺. The project will make use of the new isotope ratio mass spectrometers 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 luminescent probes to determine levels of environmentally relevant anions and reactive oxygen species (with Dr K Tuck)

Please see Kellie Tuck’s project descriptions for more information. This project is ideally suited to a student with interests in both synthetic and environmental chemistry.
More information on our research can be seen at:

Analysis of polar compounds by green aqueous normal-phase chromatography
(with Dr Reinhard Boysen and 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.

Synthesis and characterisation of molecularly-imprinted polymer films
(with Dr Lachlan Schwarz and 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.

Characterisation of PEGylated proteins and peptides
(with 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 of more effective anti-cancer drugs
(with Dr Geoff Kelso)
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 that selectively accumulate in cancer cells and disrupt fundamental metabolic pathways required for their survival.

Synthesis and characterisation of rosmarinic acid derivatives as inhibitors of platelet aggregation
(with 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. It is envisaged that at a later stage, 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.
A Practical and Eco-Friendly Method for Conversion of Epoxides to Thiiranes in continuous Flow reactor
(with Dr Shahid Kazi)

The principles of Green Chemistry are important but challenging drivers for most modern synthesis programs. To meet these challenges new flow chemistry tools are proving to be very effective by providing improved heat/mass transfer opportunities, lower solvent usage, less waste generation, hazardous compound containment, and the possibility of a 24/7 working regime to achieve multi-step synthesis of organic compounds, complex natural products and pharmaceutical agents. Thiiranes are valuable synthetic building blocks with industrial potential. They have been used advantageously in the pharmaceutical, polymer, adhesive, pesticide, and herbicide industries. In this project we will synthesize thiiranes from epoxides by an oxygen–sulfur exchange reaction in a Flow reactor.

Development of new IMAC techniques for the purification of therapeutic proteins
(with Dr Chunfang Zhang)

Bacteria can be used as factories to produce large amounts of therapeutic proteins but before being used in medicine the target protein needs to be purified from the mixture of bacterial proteins. The aim of this project is to develop new immobilized metal ion affinity chromatography (IMAC) techniques for purifying proteins using non-toxic metals, improved metal ligands and more efficient metal-binding peptide tags.

Microwave mediated synthesis of smart polymers
(with Dr Lachlan Schwarz and Dr Mahesh K Potdar)

The development of smart polymers is a rapidly growing area of material research with an incredible range of potential applications. In the past, we have successfully developed similar smart polymers to extract nutraceuticals from food waste. In this project, smart polymers capable of selectively binding a molecular target due to a designed molecular memory will be fabricated using advanced molecular modeling techniques and microwave mediated polymerization. The resulting porous polymer monoliths and monodisperse particles will then be employed for the detection and or separation of bioactive molecular targets with known therapeutic benefits from complex sources.

Novel Greener Heterogeneous Catalysts
(with Dr Mahesh K Potdar and Mr Basil Danylec)

Supported heterogeneous catalysts offer practical benefits over conventional catalysts. They are suitable for both batch and flow chemistries with potential to be a greener alternative to traditional synthesis. Triazine tethers can be used to immobilize amines to the surface of silica gel, and these cores can be manipulated to increase amino surface density. These novel materials will be prepared and their catalytic activity evaluated using classical synthetic reactions.
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. \( \text{RE} \equiv \text{ER} \) (\( \text{E} = \text{Si}, \text{Ge}, \text{Sn} \) or \( \text{Pb} \)). In this project you will prepare examples of related bulky amido substituted “metalynes” (see picture) and explore their use for the reversible reductive activation of \( \text{H}_2, \text{CO}_2, \text{NH}_3, \) 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, \( \text{CO}_2 \), to useful chemical products such as methanol.


Stabilisation and application of complexes of Group 2 metals in the +1 oxidation state. (with Dr. A. Stasch, and Dr. A. Ohlin)
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 \( \text{MgH}_2 \)). 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. The activation of other gaseous small molecules (e.g. \( \text{CO}_2, \text{N}_2, \text{NH}_3 \) etc.) will be investigated at high pressure (ca. 200 atm.) with the aid of high pressure sapphire NMR tube technology developed in the Ohlin group at Monash.

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 N₂, CO₂, H₂ 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.


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. For further information on our research group, and the chemistry we carry out, please feel free to visit our website at http://monash.edu/science/jonesgroup/
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:
http://monash.edu/science/about/schools/chemistry/staff/Langford.html

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 (with Dr J. Zhang and Emeritus Professor A. 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 (with Dr T. Bell, Dr C. McNeill (Faculty of Engineering), Dr X. Gao (Shanghai Institute of Organic Chemistry), Dr. L. Prodi (Bologna, Italy))

The overall aim of our collaboration is to develop an innovative research program to evaluate a family of novel compounds that exhibit tunable fluorescent and electrochemical properties. Using these compounds, we will study energy transduction phenomena at the macromolecular, ensemble and single molecule levels and in organic field-effect transistors (OFETs). The synthesis of dissymmetrically core-extended naphthalene diimides such as those shown below will be explored. The push-pull nature of the peripheral substituents cause naphthalene diimides of this type to display interesting photophysical and electrochemical properties.
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 and Thompson) and further afield to gain a deep understanding of how and why reactions work.

**Nucleophilic catalysis for the synthesis of pentacyclic indoles.**

Nucleophilic catalysis is a highly active area of research within our group.¹⁻⁷ 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).¹⁻³ These studies have led to the total synthesis of the β-glycoside iridoid 3.⁴

In 2014 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.

![Scheme 1](image)


**Free Radical Reaction Cascade for the synthesis of palmosalide C.**

Recently we developed a rare example of a cascade Beckwith-Dowd ring expansion/cyclisation (Scheme 2).⁸ This reaction uses materials that we have developed a range of techniques to prepare and manipulate.⁹⁻¹⁰ 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.
Reaction discovery using continuous flow immobilized catalyst beds (with Dr. T. Polyzos, CSIRO).

Continuous flow chemistry can unveil reactivity that cannot be achieved with conventional methods. In this project we are focused on immobilizing catalysts to allow heterogeneous flash chemistry to be developed. Two topics of study are currently being developed, in the first a highly chemoselective Reppe type (2 + 2 + 2) annulation will be developed. The second study focuses on the enantioselective Lewis base catalysed 1,3-dipolar cycloadditions.

Catalysis using engineer proteins (with Dr. C. Jackson, ANU)

Homogeneous small molecule catalysis can be used to access impressive structural complexity. However, a limitation of many reactions relates to the relatively high catalyst loadings required. In this project we have focused on the reconfiguration of the active sites of known enzymes for new functions, and recently accessed proteins capable of binding α,β-unsaturated ketone containing compounds (Figure 1). In this project we will examine these protein substrates interactions for the discovery of new catalytic enantioselective transformations.

11) Jackson C. J.; Lupton, D. W. Unpublished
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

**CO₂ Reduction** (with Dr Xinyi Zhang)

Depletion of our fossil fuel reserves and increasing CO₂ emissions from fossil fuel combustion are two of the most serious concerns facing humanity today. The logical solution is to use renewable energy (e.g. solar, wind etc) but the complete transition of our economy to renewable energy sources for stationary and transport applications is likely to take many decades. One exciting bridging solution is to convert CO₂ to fuels using an existing renewable energy base. We are developing advanced 3D nanomaterials for the conversion of CO₂ to fuels, therefore converting a pollution problem (CO₂ emissions) into a fuel source. The aim of the proposed project is to design, fabricate, and functionalize 3D hierarchical nanomaterials. Novel electrodes based on such materials will be used to convert carbon dioxide into fuels and valuable chemicals.

**Solar Hydrogen Generation**

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.

CO2 Absorption by Ionic Liquids (with Dr Katya Pas)

Ionic Liquids have a unique set of properties suited to the absorption of CO2 from power station flue gases as part of a carbon sequestration process. We are developing new forms of such ionic liquids for this purpose. In this project we design new ILs based on quantum calculations of the structure and binding of the CO2 complex and then prepare and test the target materials. This project would suit a student interested in both computational and practical chemistry.
The Marriott Group specializes primarily in Analytical Chemistry, and specifically Separation Science/chromatographic methodology, supported by a broad cohort of applications studies. We develop new methods in GC, including comprehensive two-dimensional GC (GC×GC), and multidimensional GC (MDGC), using a range of specific detection technologies, including mass spectrometry. In 2013, two triple quadrupole MS systems were delivered; we have access to a Q-TOFMS. These transform our studies, and with our MDGC research we now lead 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. Applications 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 technology**

GC and HPLC are key tools for illicit drugs analysis. We have proposed new methods for drugs profiling based on the demonstrated capabilities of GC×GC. We applied this technology to analysis of steroids relevant to the World Anti-doping Agency (WADA), achieving detection parameters required by WADA for detection of key steroids in urine. Rather than use selected ion monitoring (SIM) methods required in conventional GC, we now full scan mass spectrometry, with many advantages for the routine analysis of drugs of abuse: (i) better spectral matching and confirmation of the compound; (ii) the 2D separation space 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 / re-interrogation of the result for evidence new designer drugs should they be discovered in future. 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 have good experience in sports steroids analysis, and in 2013, we will investigate beta-2 agonists and some other banned class of drugs during sports, to extend the method to other drugs on the WADA list, and this can include benzodiazepines, stimulants, and a variety of classes of compounds 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. This figure shows the use of GC×GC for heroin profiling, and illustrates the very comprehensive profiling that is possible with this technique, translating to better knowledge of sample composition.
Methods for Fatty Acids (FAME) characterization in soils: validation of analytical extraction and derivatisation, investigated by GC and Mass spectrometry methods.

Fatty acids analysis plays an important role in establishing the levels and heterogeneity of this class of compounds in many sample types. There is a continuing need to improve detection and separation of individual structural isomers within this class of compounds, because only by improved separation can we have improved certainty of the identity of each compound – whether it be for degree of unsaturation, positions of double bonds, branching, presence of hydroxylated derivatives, and cyclic structures. In the present study in collaboration with Prof Tony Patti, we will validate the methods use for sample extraction and derivatisation, and then undertake a GCMS procedure for improved characterisation of the FAME products.

We have previously applied GCxGC to a range of saturated and unsaturated FAME, but now need to extend this to the other derivative types. We also wish to extend the capabilities for FAME analysis to MDGC methods, which we believe will establish a new protocol for FAME analysis.

By use of prep GC and MDGC methods for this, we can isolate individual compounds and ideally deduce the chemical structure of the compound using spectroscopic methods not available to the GC method. Here we show that classical GC (upper panel) does not resolve the FAME well. The modulated method (middle) increases the signal magnitude, and when transformed to a 2D plot, improved separation is clearly achieved.

Ionic liquids (IL) and other novel phases in capillary GC. Retention characterisation, applications and design of advanced separation strategies.

A range of recently introduced stationary phases have become available for high resolution GC chemical separation. Through the support of Sigma-Aldrich, we have access to all the commercially-available IL column phases – which come in the designations IL59, IL60, IL61, IL76, IL82, IL100 and IL111 – in a variety of dimensions. These descriptors are according to relative phase ‘polarities’, based on McReynold’s constants. IL111 is one of the most polar GC phases available. The IL columns offer interesting selectivity towards fatty acid methyl ester (FAME) isomer separation, and we have investigated a number of relationships for FAME interaction with IL phases (Zeng et al. Anal. Chim. Acta (2013) in press. http://dx.doi.org/10.1016/j.aca.2013.07.002).

One of the more advanced interpretations of separation and interaction between phase and solute is the use of Abraham descriptors. These can quantify relative retentions of compounds, and offer a means to prediction of separations. Ultimately, it should be possible to also predict and simulate various experimental results for compounds using a database of Abraham descriptors.

We have also started to use these phases in a range of applications, amongst which include FAME analysis. In this study, we will explore a range of IL phases for their retention performance towards a series of compounds of various chemical classes, seek to understand how retention behaviour can be modeled by using Abraham molecular descriptors, and then implement an advanced two-dimensional separation method that can provide the best-case scenario for maximised separation based on simulation and experimental evidence.
This document will give you an idea of some of the research we are undertaking within my group. Although I will not return from sabbatical until January, 2014, feel free to email me to discuss these projects in more detail. More information on my research can be seen at: http://monash.edu/science/about/schools/chemistry/staff/martin.html

Synergism – an effective strategy to combat multidrug-resistant bacterial infections
(with Dr Cornelia Landersdorfer, Pharmacy & Pharmaceutical Sciences).

The rapid increase in bacterial resistance is one of the ‘top 3’ most serious threats to global health. In particular, the Gram-negative ‘superbugs’ Pseudomonas aeruginosa, Acinetobacter baumannii and Klebsiella pneumoniae are exceptionally capable to become resistant to virtually all available antibiotics in monotherapy. No new antibiotics against these critical Gram-negative bacteria will become available for many years to come and modern medicine is at risk of reverting to a pre-antibiotic era!

Rationally designed synergistic combinations of available antibiotics present a highly promising and timely opportunity to combat multidrug-resistant bacteria. However, in order to develop these treatments, a fundamental understanding of the mechanisms of synergy is needed to maximise bacterial killing, minimise resistance and minimise the toxicity of the antibiotics, thus enable a novel and effective antibiotic dosing strategy to be developed. Synergism is defined as a joint action of two drugs in such a manner that one enhances the action of the other to produce an effect greater than that which may be obtained with either one of the drugs in equivalent quantity or produce effects that could not be obtained with any safe quantity of either drug, or both. Thus, lower doses of two drugs are more effective than the best response of each alone!!

Some antibiotics have intracellular targets, however, the extracellular disruption of the bacterial outer membrane can also be important, limiting the permeability of most antibiotics or compromising bacterial integrity. This mechanism has attracted much less scientific attention, but is critical. This project explores the membrane penetration properties of two classes of antibacterial drugs ‘in isolation’ and ‘in synergy’ using several biophysical methods1. In particular, their membrane penetration properties alone, or in combination will be examined at biomimetic membranes. The preliminary pharmaceutical results show that they kill bacteria more effectively when used in combination2, however, it is necessary to understand the mechanistic steps that underlie the pharmacological activity in order to optimise combination therapy.


Molecular Dynamics and Study of the Evolution of Protein Function (with Dr Ashley Buckle, Faculty of Medicine, NHS and Ray Rodgers, Faculty of Medicine, University of Adelaide).

The biomolecules that define life at the cellular level are proteins. They are involved in a myriad of dynamic behaviours including protein-protein interactions that support functionally active complexes. In the last few decades structural biology (X-ray, NMR, SAX, synchrotron methods) has provided well-defined molecular structures although these do not always provide functional information. This has lead to many advances in medicine. However, we are now entering a new era of systems biology, in which we need to understand how proteins move and interact in space and time. Approximately, 40% of the human proteome is known to be ‘disordered’ or conformationally heterogeneous, being constantly dynamic rather than having a static or
fixed structure. Importantly, many of these dynamic molecules are drug targets, hence, important to understand.

Nature has a number of natural born mutants containing polymorphisms or even duplication of genes with evolutionary consequences; although in many cases these are not identified until diseases or phenotypes are found. We recently, examined the CYP19 gene, responsible for expression of the enzyme cytochrome P450 aromatase. This enzyme is responsible for oestrogen biosynthesis from androgens. Among mammals there is only one CYP19 gene, and one gene product (enzyme), except pigs – which have three isozymes; gonadal, placental and blastocyst. The amino acid sequences of these P450arom enzymes are similar, although their activities differ dramatically. The isozymes evolved from gene duplication over 300,000 years ago. Yet despite the closeness of pigs in an evolutionary sense, the functional significance of these isozymes is not known.

This project will data-mine the sequences for a number of important steroidogenic P450 enzymes, to examine the importance of the natural born mutations. The expression of these mutations and comparison of their biochemical and biophysical properties the these mutations, among species will be explored. Students with a mathematics or bioinformatics will be well suited for this project.

Can Alzheimer’s Disease be reversed? (with Dr Anthony O’Mullane, RMIT and Dr John Carver, ANU).

A number of neurological diseases are linked to protein/peptide aggregation including Alzheimer’s Disease (AD) and Parkinson’s Disease. In fact, ~70% of all late-onset dementia cases are due to AD and with an aging population in Australia, intense research is therefore required to find better therapeutic approaches. Although there are several treatments available for AD, these can only manage the disease and offer no reversal, hence there is no cure. Also, for diabetes, aggregation of peptides in the pancreas; human islet amyloid polypeptide (hIAPP) can occur. Thus, a fundamental molecular knowledge to control peptide aggregation is urgently needed.

There is some evidence that treatment with polyphenol’s can prevent aggregation of the major aggregating peptide in AD, the amyloid β peptide (or Aβ). We have found that a non-disease, aggregating peptide could dis-aggregate, so the process can be reversed! Also, the mode of action towards biomimetic membranes had some similarities to antimicrobial peptides and this activity could be stopped in the presence of polyphenols, or related peptides. This project aims to investigate the basic interactions that lead to peptide aggregation, explore a range of ways in which aggregation can be controlled or prevented and investigate the impact of aggregation process on the membrane layer.
Vibrational spectroscopy of C₆₀ – Buckyballs in space.

C₆₀ was discovered through experiments aimed at obtaining spectra of long chain carbon molecules thought to be abundant in the interstellar medium resulted in Nobel prizes for Kroto, Smalley and Curl. Kroto speculated that C₆₀ should be abundant in interstellar space and recently IR emission bands in the constellation Ara were discovered that correlate well with the 4 bands of the highly symmetric buckyball (see figure) and seem to confirm this speculation. These spectra are compared currently with IR spectra of solid C₆₀ and in order to confirm this assignment gas phase spectra of buckyballs are required. In this project we will generate buckyballs by infrared laser pyrolysis of ethylene (ethene) directly in a multipass gas cell on a spectrometer located at the Australian synchrotron. Ethylene has a strong absorption at the same frequency as that generated by a CO₂ laser so direct absorbance of the laser provides an energy source high enough to generate buckyballs in situ. During the experiment we also follow spectroscopically the processes leading to the formation of C₆₀.

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 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.

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

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Room No. 228, Tel: 9905 9362, email: Chris.Thompson@monash.edu
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. The project will require close collaboration with the school of biological sciences, where the microalgae will be grown and the use of GC and mass spectroscopy analytical techniques.

Raman spectrum of a single 2 micron diameter microalgal cell.
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:
http://monash.edu/science/about/schools/chemistry/staff/murray.html

Synthesis and Magnetostructural Investigations of Mononuclear and Polynuclear Spin Crossover Compounds of Iron and Cobalt (with Professor S. 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) and Dr Ian Gass are currently extending our study of spin crossover and supramolecular systems of the cluster and 1D types, including Fe and Co–organic radical systems. Their work has yielded major publications in 2013 (below a Fig. from *Dalton Trans*. 2013 of a “crown” ligand). The choice of ligand and/or their substituents are of paramount importance in obtaining spin crossover behaviour, so that organic synthesis, with good input from Christopher Gartshore, (R.A.), 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 Professor Jean-François Létard (Bordeaux, France). Synchrotron crystal and powder diffraction studies are made, across the road, at the Australian synchrotron. Prof Cameron Kepert and Dr Suzanne Neville (Sydney) collaborate on nanoparticle spin crossover work, structure and synthesis of extended framework crossover systems.

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.** (with Professor S. Batten)

(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), Daniel Wielechowski and Crystal Le (Chemistry undergraduates) are successfully using ligands such as N(CH$_2$CH$_2$OH)$_3$ to make a range of beautiful clusters with very interesting properties. We collaborate with Professor Chibotaru (Belgium) and Dr Rajaraman (India) on theory. Daniel and Stuart have just had a $\{\text{Cr}_2\text{Dy}_2\}$ SMM cluster accepted by one of the world’s top journal *Angew. Chem. Int. Ed.*

(b) The second, separate project is to make new examples of polycyano-bridged metal frameworks and clusters, including lanthanide species, using the ligand types shown below, studied by Professor Stuart Batten, David Turner (Future Fellow) and Ponco Prananto (PhD student) (a recent Dy$_8$ paper is in *Dalton Trans*. 2012, **41**, 3751):
Water splitting using niobium stabilised nano-catalysts (with Dr Jie Zhang)
We’re currently facing the choice between an energy crisis and an environmental one -- while current reserves of fossil fuels, in particular coal, will last through most of the 21st century, the environmental penalty of using them will be severe. There’s no shortage of alternative fuel sources, such as solar and wind energy, but storing the generated electricity is a challenge.

The best solution is to store the energy in the form of hydrogen by using the electricity to electrolyse water in the presence of a catalyst. This honours project aims to develop new electro-catalysts for splitting water into hydrogen and oxygen.

A common problem with redox catalysts is that they often incorporate organic ligands which are in particular sensitive to oxidation. By doing away with these and replacing them with inorganic ligands in high oxidation states, the stability of the catalysts can be improved, and by harnessing the properties of niobium, the catalyst can be stabilised at elevated pH.

This honours project will involve inorganic synthesis, synthesis of nanoparticles, electrochemically driven water splitting catalysis and characterisation of the catalyst.

For more information contact Andy Ohlin or Jie Zhang (jie.zhang@monash.edu). See also http://monash.edu/science/about/schools/chemistry/staff/ohlin.html
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Development of new electrolytes for lithium-ion batteries

Traditional molecular solvents such as acetonitrile and ethylene carbonate are widely used as organic electrolytes (OLs) 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 traditional OLs, 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 technologies. Recently we showed that the Fragment Molecular Orbital (FMO) approach combined with the MP2 level of \textit{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. (\textit{Chem. Commun.}, 2012, 48, 1493). Coupled with the molecular dynamics (MD) formalism, this \textit{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 a number of computational packages, including GAMESS-US, and will perform FMO-MD calculations of combined IL and OL clusters of varying size on our new 512-core Dell Cluster located 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 \textit{ab initio} molecular dynamics simulations of proton and electron transfer processes.”

Prediction of reduction potentials of metal ions in ionic liquids

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 a computational package, GAMESS-US, will perform FMO-MD calculations our new 512-core Dell Cluster located 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”.

Development of the FMO approach for protic ionic liquids

Protic ionic liquids (PILs) are ionic liquids obtained by proton transfer from a Brønsted acid to a Brønsted base. The very first ionic liquid synthesized by Paul Walden was in fact a protic ionic liquid obtained by ethylamine with nitric acid. The striking difference between PILs and aprotic ILs discussed above is the ability of the former to form extended hydrogen bonding network. This network enables the transferred proton to become rather mobile, thus making the PIL proton conductive without any water present! It is not surprising that protic ionic liquids have found application as proton conducting electrolytes in fuel cells. (e.g. see T. Yasuda & M. Watanabe, MRS Bulletin, 2013, 38, 560-566). The hydrogen-bonding network represents a challenge for the fragment molecular orbital approach as the system might not be potentially treated accurately enough using two- and three-body types of interactions that work exceptionally well for aprotic ionic liquids. A similar situation is observed in liquid water, in which the cooperative effect of intermolecular interactions extends beyond five water molecules. In this project the student will investigate the importance of four- and five-body interactions for larger clusters of protic ionic liquids comprised of typical cations and anions used in the field. The student will also test a modified version of the MP2 method that has been recently developed in our group. This modified MP2 method gives very high accuracy for energetics of aprotic ionic liquids. The student will learn how to use a number of computational packages, including GAMESS-US, and will perform FMO-MP2 calculations on our new 512-core Dell Cluster located at the Monash e-Research Centre. This project will be done under the ARC Future Fellowship entitled “Towards ab initio molecular dynamics simulations of proton and electron transfer processes”.

![Figure 3](image3.png)

**Figure 3.** Comparison of electrochemical windows of ionic liquids (black curve) and water (red curve).

![Figure 4](image4.png)

**Figure 4.** Example of PIL, ethylammonium acetate
Chemical Conversions of Lignocellulose Biomass

Fine chemicals from biomass waste (with Professors Roy Jackson and Doug MacFarlane)
The use of biomass to derive fine chemicals and fuels 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 derivatives.

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.

Lignin Depolymerisation (with Dr Kei Saito – see entry under Dr Kei Saito)
Lignin, a stable and insoluble polymer, composes 30% of wood tissue, and is produced by the oxidative polymerization of phenol derivatives catalyzed by laccase, an enzyme in nature. Utilising a model polymer (polyphenylene oxide) Dr Saito was able to demonstrate the depolymerization of this lignin analogue in water. This project will investigate the depolymerization of lignin derived from biomass, leading to potential useful building blocks for biodegradable polymers.

Use of Ionic Liquids for Selective Extraction of soil organic matter, biomass and other natural organic materials (with Professors Alan Chaffee and Doug MacFarlane)

Ionic liquids offer potential for the selective extraction of particular fractions of soil organic matter and biomass, including lignin, cellulose, 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 fractionation into different classes of material. Ionic liquids can also be used to selectively separate different organic polymers from their natural matrix (e.g., cellulose and lignin). This project will involve the extraction of soil or biomass with a range of selected ionic liquids, and the subsequent chemical evaluation of the organic matter extracted and recovery of the ionic liquids.

Soil Organic Matter, Soil Carbon Sequestration, Organic-based Fertilisers and Soil Fertility (with Professors Roy Jackson and Alan Chaffee and Dr Tim Cavagnaro)

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 biochars). An area of growing interest is also the potential for agricultural uses of by-products originating from biomass thermal treatments (eg to produce bio-oils/fuel).

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 biomass waste streams; chemical composition of litter inputs in forested areas and its decomposition/transformations in soil. Soil-plant interactions in the presence of selected amendments and/or fertilisers 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.

**Fatty Acid Methyl Ester (FAME) characterization in soils: validation of analytical extraction and derivatisation, investigated by GC and Mass spectrometry methods** (with Professor Philip Marriott and Dr Tim Cavagnaro) - see entry under Professor Philip Marriott

Fatty acids derived from phospholipids in soil are commonly used as markers to evaluate the distribution of soil microbial populations. This information is important in the understanding of impacts of external factors (e.g fertiliser use, drought, climate effects) on soil properties and soil health. This project with Prof Phil Marriott and Dr Tim Cavagnaro, will validate the methods used for sample extraction and derivatisation, and then undertake a GCMS study for improved characterisation of the FAME products.

**Catalytic Wet Air Oxidation (CWAO) (with Professor Leone Spiccia)**

The development of benign, versatile catalysts that can be used for both selective oxidations and/or capable of decomposing organic contaminants, pollutants, and harmful microorganisms is needed for various applications. Both photocatalysts and redox catalysts have been used independently, but there are fewer examples which combine both activities. Recent work has shown that catalysts comprising a mixture of manganese and cerium oxides show both redox and photocatalytic activity. For example, the conversion of 5-hydroxymethyl furfural to the dialdehyde (see below) was undertaken in 97% yield with a MnCeOx catalyst in the presence of air and light.

![5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxaldehyde (FDA)](image)

This project will attempt to synthesise and characterise oxides which combine both photo- and redox catalytic properties. These will be tested as oxidation catalysts against a range of common classes of organic compounds.
Our group’s research interests cover a wide range of disciplines all involving the design, synthesis and evaluation of *smart molecules*. Programs include total synthesis, synthetic method development, chemical biology, medicinal chemistry and new technologies. Some potential projects for Honours 2014 are briefly described below. More information on our research can be seen at: www.chem.monash.edu.au/staff/perlmutter/index.html. We have active collaborations with many groups locally in Medicine, Engineering and Science at Monash, Univ. of Melbourne and RMIT Univ. (as well as interstate (ANSTO) and overseas (Univ. of Oxford, UC San Diego, Univ of Tromsø, Univ. of Hyderabad, Shanghai Institute of Organic Chemistry).

**Total synthesis of Steroids.**

*Steroids* are one of the most important classes of chemical therapeutics accounting for approximately one third of pharmaceuticals sold globally. Remarkably there are very few economical methods for making steroids including, especially, new steroid libraries. We have recently developed a new approach to steroid synthesis which involves cycloaddition of our recently synthesized semi-cyclic dienes such as **2** with doubly-activated dienophiles such as **3**. We have found that these reactions proceed efficiently, however we need to improve the diastereoselectivity. Once prepared the adducts (eg **4**) can be transformed into steroids in a few short steps.

**Total synthesis of the Zaragozic Acids.** The *Zaragozic acids* potent inhibitors of squalene synthase. We are developing a new route to the *Zaragozic acids* based on stereoselective reductive and/or oxidative couplings of α-keto-esters. Remarkably little is known about such couplings intramolecularly and there is much exploration ahead in this field.

**Understanding adaptive immunity at a molecular level** (with Professors Rossjohn, Monash and D Godfrey, Melbourne).

Recently Borg et al published the first X-ray crystal structure of a CD1d-Ag complex (Ag = α-GalCer) bound to its T cell receptor NKT-TCR. This structure provided some profound insights into the way in which the TCR recognizes the antigen bound to its presenting cell (CD1d). In order to gain a deeper understanding of these interactions we will prepare series of analogues of known glycolipid antigens such as α-GalCer and evaluate their affinity for CD1d. We will also prepare CD1d-Ag complexes and determine their three dimensional structures.
Self-assembling fibres (with Professor Aguilar, Monash and Dr. Adam Mechler, La Trobe Univ.). We have designed small, synthetic helical peptides which spontaneously self-assemble to form fibres ranging in size from nano- to macro-scale. The peptide monomers self-assemble in a unique head-to-tail fashion which is driven by a 3-point H-bond motif associated with the 14-helical structure of N-acetyl-β3-peptides. This provides extraordinary opportunities for designing new materials with functionality located along these faces. Perhaps even more significant, is that the perfect pitch offers the opportunity to design a supramolecular self-assembly motif to link the monomers in a highly symmetrical manner reminiscent of one dimensional crystallization. The inherent flexibility, as well as ease of synthesis, provides new avenues for the development of novel nanomaterials for application across medicine and engineering.

Surface acoustic wave accelerated chemistry (with Assoc. Professor Friend and Dr Yeo, Monash Engineering).

Surface acoustic waves (SAWs) are 10 nm amplitude electroacoustic flexural waves, that propagate along the surface of a piezoelectric substrate (chip). With SAWs one can, in principle, move droplets to an xy address on a chip (droplet translation), activate and accelerate the chemical process (our own work), remove any solvent (atomisation) and move the droplet to a new xy address for removal and/or further reaction. Consequently SAW-based chemistry offers the potential for a complete technology for chemical synthesis based on one energy source. Very recently we have demonstrated the use of SAWs in several important chemical processes, including nucleophilic addition, condensation, catalysis, cycloaddition, tetramerisation. Reaction times are usually (ie 1-10 minutes) and are highly energy efficient. In this project we will develop further this technology extending the design of the device as well as the frequencies employed in order to further enhance the usefulness and energy efficiency of the technology.

Exploiting new [3,3]-sigmatropic rearrangements.

We have begun a program, based on the use of the [3,3]-sigmatropic rearrangement of diaeyldyrazines (eg 5) to generate several new important classes of compounds. For example we have discovered that carrying out a Curtius rearrangement on acid-amides derived from the sigmatropic rearrangement products leads to a very facile synthesis of new, chiral pyrimidine-2-ones (eg 6) via intramolecular trapping of the intermediate isocyanate with the adjacent N-methylamide (a reaction with little literature precedent). The products are chiral analogues of the pyrimidine nucleobases, cytosine, thymine and uracil, and there is obviously significant scope to expand this discovery in the field of nucleic acid chemistry as well as anti-viral therapy.
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).

Catalysis
Our group has a long standing interest in catalysis, particularly when it is applied to asymmetric synthesis, natural products and peptidomimetics. We are currently interested in the synthesis of new ligands and catalysts, developing efficient tandem catalytic processes for organic transformations and industrial feedstocks, and the application of catalysis to bioactive targets and natural products. We have many active projects in this area.

For example, Mr Nic Spiccia (PhD 2009-) has been investigating the synthesis of lepadiformine and Mr James Wang (PhD 2010-) has been investigating a catalytic approach to bioactive spirocyclic alkaloids such as cylindricine. With the use of olefin metathesis, and close examination of the catalytic cycle, a concise, high yielding route to homologous spirocyclic pyrrolidines and piperidines has been developed. This work has resulted in extending the utility of olefin cross metathesis to highly hindered olefinic substrates.

Cyclic peptides
Nature uses cyclisation to protect peptide backbones from proteolytic cleavage. Unstable cystine bridges can be replaced with non-proteinaceous dicarba linkages. Using tandem catalytic sequences and specially designed non-proteinaceous amino acids, we have developed a way to control the formation of three dicarba-bridges. We have several projects examining the preparation of carbocyclic derivatives of naturally occurring cystine containing molecules, including conotoxins (see CtxIMI below), biologically active peptide neurotoxins produced by Conus marine shells (with Professors Ray Norton (Monash-Parkville) and David Adams (RMIT)), cyclotides and somatostatin derivatives. Selective alkene and alkyne metathesis routes are currently being explored as a route to complex biologically active toxins. Mr Simon Gooding (PhD, 2008-) is currently investigating a new way of combining alkene and alkyne metathesis to achieve regioselective C-C bond formation.
**Insulin superfamily**

One important class of disulfide containing peptides is the insulin super family, which includes, insulin, relaxin and a number of insulin-like growth factors (IGFs). These peptides are involved in important biological functions such as glucose metabolism and partuition where several disulfide bonds are formed but whose specific function in the resultant biological function remains unknown. Several projects aimed at elucidating the structural versus functional role of cystine motifs in these proteins are available in 2012.

We have already made significant progress in this area and have synthesised and tested several highly promising insulin analogues which display equipotent metabolic activity to human insulin, reduced mitogenic potential (via IGF receptor activation) and high physical stability. This is a great start! Over 200 million people have diabetes, and it is widely considered to be the world’s fastest growing disease. Diabetes is a chronic disease, characterised by the onset of hyperglycaemia, which is maintained through the use of insulin. How insulin activates its receptor is still unknown...a great mystery just waiting to be solved! A project in this area would involve organic synthesis, catalysis and peptide synthesis and purification. Structural characterisation of new insulins will be performed in collaboration with Prof Ray Norton (Monash Parkville) and biological testing will be performed by an established biological team including Dr Sof Andrikopoulos (U of Melb) and Dr Briony Forbes (U of Adel). *Dr Bianca van Lierop* (PhD 2012) recently developed methodology to facilitate the synthesis of novel insulin super family analogues (shown at right, A chain (yellow, top) and B chain (magenta, bottom)) possessing significant biological activity and has paved the way to some exciting discoveries to come.

**Thermochromic fibres for wound monitoring**

Temperature-sensitive fibres and textiles can be applied to a variety of thermal mapping applications such as wound monitoring (e.g. leg ulcers, chronic wounds, diabetic foot). In collaboration with CSIRO, *Ms Louise van der Werff* (PhD 2009-) has recently developed a three layered composite fibre composed of a liquid crystalline layer encapsulated between a transparent polypropylene outer sheath and a black polyether ketone inner core (images left). The fibres exhibit clear thermochromic behaviour within the body temperature range and can be knitted into textiles (images right). Projects extending this work will be available.
Dr Kei Saito
Room No. 213/Bldg 75, Tel: 9905 4600, email: Kei.Saito@monash.edu

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/

Self-healing Polymers (with Professor George Simon, Materials 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 and photo self-healing epoxy and acrylic resin using several cross-linkers with reversible units. This project will involve aspect of organic synthesis, polymer synthesis and polymer characterization techniques.


Developing a Novel Polymer Recycling System

Solid-Crystalline Photoreversible Polymerization

_Reverseable polymers_ are polymers in which bonds can be easily broken. Most conventional polymers are structurally irreversible because their monomer units are connected by strong covalent bonds. Reversible polymers have a reversible bond within their structure that can be formed from the monomer units and cleaved back to the monomer units by heat or light. Such novel polymers are of interest because of their potential applications as recyclable environmentally benign materials, photo-resists, and biomedical materials.

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.

Lignin Degradation and its Biomass Application (with: Assoc. Professor Tony Patti)

Lignin, which composes 30 % of wood tissue, is produced by the oxidative polymerization of phenol derivatives (coniferyl alcohol) catalyzed by laccase, an enzyme in nature. Lignin is known as a stable and insoluble polymer and the disposal and recycle of lignin has been a big resolved issue for the paper industry. Poly(2,6-dimethyl-1,4-phenylene oxide) has been depolymerized using quinone ketal redistribution mechanism. It can depolymerize by mixing the polymer with 2,6-dimethylphenol monomer. The formed oligomer could repolymerize using oxidative polymerization. Lignin has a same poly(phenyleneoxide) backbone in their network and we would like to extent this method to Lignin. The formed lignin oligomer will polymerize to form a biomass plastic. The aim of this project is to depolymerize lignin in water using redistribution mechanism to investigate a new recycle system for lignin. Depolymerization of lignin to a repolymerization has an apparent great advantage as a sustainable technology in the development of green chemistry.

Discovering Block Co- and Terpolymers for Antibacterial Film using Living Polymerization Techniques

Bioinspired mechanisms are being used to create alternatives materials using the principles of green chemistry. Deriving inspiration from the biological mechanism, novel water insoluble antibacterial film from crosslinkable block copolymers 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.


Ionic Liquid Polymer Syntheses (with Dr. Jie Zhang)

Ionic liquids (ILs) are generally defined as organic/inorganic salts with a melting point lower than 100 °C which present a good chemical and electrochemical stability, low flammability, negligible vapour pressure and high ionic conductivity. Although originally, most of the research and industrial activities related to ILs were associated to their applications in green chemistry. Combining ILs with polymer electrolytes offers the prospect of new applications e.g. in batteries and fuel cells, where they surpass the performance of conventional media such as organic solvents (in batteries) or water (in polymer electrolyte membrane fuel cells), giving advantages in terms of improved safety and a higher operating temperature range. We will focus on developing and synthesizing IL polymers and applying those as electrode.
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, legislating significant emission reductions or introducing measures such as carbon pricing. The Honours Projects described below focus on the conversion of solar energy into either electricity or fuels.

Dye sensitised solar cells (DSCs)
DSCs are viable alternatives to ‘classical’ photovoltaics. They typically consist of a nanostructured titania film coated with a monolayer of photoactive dye and an electrolyte containing a redox couple (normally iodide/triiodide, $I_3^-/I^-$). We are developing new non-volatile, non-toxic redox couples while at the same time trying to improve the efficiency and long-term stability of DSCs. We have applied ferrocene and cobalt complexes as replacements for the very corrosive $I_3^-/I^-$ redox couple (Daeneke et al., *Nature Chem.*, 2011, 3, 211, Khashif, et al, *Angew Chem.*, 2013, 52, 5527). 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, Xiang et al, *Energy Environ Sci.*, 2013, 6, 121). In an Honours project, we would like to develop new ionic liquid, plastic crystal and/or water based DSCs electrolytes which incorporate the less corrosive ferrocene redox couples and a wide variety of transition metal complexes. We are also interested in pursuing the development of perovskite DSCs which have recently achieved 15% efficiency.

Solar Hydrogen
Hydrogen is considered the ideal clean fuel for the future and achieving the “Hydrogen Economy” is an ambitious international goal. When burned in fuel cells in the presence of oxygen, it produces energy and 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 catalysts, made from earth abundant elements. 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 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 below) 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 studies have, however, revealed that the actual water oxidation catalyst is a manganese oxide mineral and not the Mn cluster (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 solar water splitting devices.

**New Agents for the Treatment of HIV** (with Associate Professor 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 found that these molecules not only bind to mRNA, they also cleave it (Org. Biomol. Chem., 2009, 7, 30). Thus, its should be possible to develop potent agents that inhibit replication by cleaving RNA rather simply binding to it. 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 target RNAs (J. Am. Chem. Soc., 2009, 131, 1106). One issue impacting on the application of these conjugates is the ability to pass through cell membranes where they can act on the target biomolecule. Assoc. Professor Martin and her group have developed techniques for the in vitro measurement of membrane permeability of biomolecules (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, Germany).

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 (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 and upconverting 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, macrocyclic ligands that allow for the introduction of a radioisotope (e.g., $^{64}$Cu/$^{67}$Cu) and photoactive ruthenium complexes to allow for fluorescence imaging (J. Am. Chem. Soc., 2012, 134, 20376).
These research topics in inorganic and organometallic chemistry focus on molecules with elements in rare oxidation states, unusually bonded fragments and rare metal hydrides. 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 novel anionic iminophosphoranes and related N-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 novel compound classes with new functionalities and reactivity. Very recently, we have prepared new diiminophosphinate ligands that typically form 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 chemistry of these and related ligands 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.

![Chemical structure](image)


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

Recently we have prepared the first stable magnesium(I) compounds with the general formula LMgMgL (L = monoanionic ligand). These easy to synthesize, ‘bottleable’ and hydrocarbon soluble reduced magnesium complexes can act as very selective reductants for organic substrates. 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. These are typically not accessible using ‘classical’ reducing agents such as Na, K, KC₈ 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 Al₂H₄, Ge₂ (see picture, Ge: red, N, blue, C, grey), and Sn₂. Your project will include the preparation of new and known metal complexes using common NHC

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

The ionic or ‘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. Soluble, well defined metal hydride complexes of the alkali metals are very rare and limited to few Li examples despite their potential importance for hydrogen storage and other technologies due to their high hydrogen content. 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 Li8H45+ metal hydride core is protected by four sterically demanding phosphinoamide ligands developed by us. The presented LiH complex has been shown to 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- and O-ligands to assemble small and large metal hydride complexes and investigate their properties and reactivity. See: 1: S. Harder, *Chem. Commun.* 2012, 48, 11165; 2: A. Stasch, *Angew. Chem. Int. Ed.* 2012, 51, 1930.

**Synthesis, structure and reactivity of molecular group 2 metal hydride complexes**

(with Professor 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.* MgH2, CaH2). Also, these sought after complexes are of considerable interest for hydrogen storage technologies. Your project will involve the development of new metal hydride complexes, incl. large metal hydride clusters, 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. Éd.* 2008, 47, 9079; S.J. Bonyhady *et al.*, *Chem. Eur. J.* 2010, 16, 938; S. Harder, *Chem. Commun.* 2012, 48, 11165 (a review).
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. Our projects often involve collaboration with other groups at Monash, in Australia and overseas, and often encompass trips to large-scale facilities such as the Australian Synchrotron and the Bragg Institute.

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*.

**New environmentally-friendly stabilisers for emulsions and foams**

One of the biggest issues facing scientists at the present time is how to make the resources for our chemicals and products sustainable. Surfactants and stabilisers are everywhere – from laundry detergent to paint to ice-cream. However, many of these molecules are derived unsustainably from crude oil. A growing challenge is to find equally effective replacement molecules that can perform the same tasks – of stabilisation, lubrication, dispersion, *etc.* – but that come from renewable sources.

In this project, you will discover and develop a range of new stabilisers from environmentally-renewable sources – molecules from biological feed-stocks and biologically-derived particles. You will test the properties of these stabilisers in various systems including at air-liquid and liquid-liquid interfaces. We have a range of methods for measuring the properties of such materials, from tensiometry to AFM, scattering and microscopy. Monodisperse emulsions can be made very reproducibly using microfluidics, in order to easily compare the properties and effectiveness of different systems. Once you have uncovered the properties of your benign stabilisers, you will explore the best ways to deploy them to make a new range of biodegradable emulsions and foams. This project may involve trips to the Australian Synchrotron and the Bragg Institute (Sydney).
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 synthesise and analyse the photochemical properties of newly-designed molecules based on fluorescent cores. 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, you 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 biophysical and 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.

Electronic control of drops and colloids

Using electric and magnetic fields to control colloidal drops, particles and bubbles involves fascinating fundamental phenomena, and is also the basis for many cutting edge technologies: for example, the lens in some smart phone cameras is a liquid droplet that changes its shape with applied voltage, and the displays in eBook readers are made from electro-responsive particles.

In this project, you will use electronic fields to control and manipulate colloids in new ways, with the aim of developing novel devices. Our particular focus is on control of droplets, and how ultra-low voltages and currents can change droplet shapes and move colloids. This project is adaptable, from focusing on surface chemistry and charging mechanisms, to developing and programming new devices and instruments, depending on your interest.

Through the course of the project, you will use existing methods for exploring how fields affect colloids, including AFM and tensiometry, but you will also develop new approaches based on interferometry and the scattering of light.

Materials from graphene – from liquid crystals to sensors

Few materials have generated as much interest as graphene – single sheets of carbon atoms with remarkable electronic and mechanical properties. We have recently been exploring how graphene behaves in liquid environments and at interfaces, as this may provide new methods for processing and functionalising it, as well as providing 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.

This project will develop skills in AFM, microscopy and materials chemistry. In addition, it may involve scattering experiments at the Australian Synchrotron and the Bragg Institute (Sydney).
Developing luminescent probes to determine levels of environmentally relevant cations and reactive oxygen species (with Assoc. Professor Mike Grace)

1/ Environmentally relevant cations

High concentrations of Zn\(^{2+}\) and Hg\(^{2+}\) can cause severe environmental problems in our waterways. Quantification of both of these cations in environmental samples is problematic. For Zn\(^{2+}\), conventional testing measures the total concentration of zinc, rather than the bioavailable Zn\(^{2+}\). There is also no straightforward way of measuring the concentration of Hg\(^{2+}\) in environmental samples. Recently we have used novel, luminescent based chemosensors to detect toxic concentrations of Zn\(^{2+}\) in environmental samples. Our lanthanide based chemosensors have an organic chelate and an ‘ntenna (Fig. 1). When the analyte of interest binds, and a time delay is introduced, background fluorescence and scattered light decay become negligible. The resulting luminescent signal is dependent only on the concentration of the luminescent probe and the target ion. Our previously synthesized sensors show good selectivity for Zn\(^{2+}\) over other cations, however, their luminescent properties and selectivity need improvement. We also wish to apply this class of sensors to the detection of Hg\(^{2+}\) in environmental samples.

This project will involve the synthesis and testing of this exciting new class of luminescent probes with the goal of determining the levels of Hg\(^{2+}\) and Zn\(^{2+}\) in several Melbourne wetlands.

![Figure 1](image.png)

**Figure 1** The action of lanthanide based sensors, this diagram depicts the binding of Zn\(^{2+}\).


2/ Reactive Oxygen Species

Reactive oxygen species (ROS) are present in low concentrations in seawater and it has been reported that a number of algal species can increase their production of ROS under stressful conditions. ROS include; hydrogen peroxide, singlet oxygen, superoxide, hydroxyl radicals and hypochlorite. We are looking at developing a lanthanide based sensor for ROS. This lanthanide sensor contains an organic chelate, an antenna as well as a quencher group. Once the lanthanide sensor reacts with the ROS the covalent bond between the quencher group and the antenna will cleave and a luminescent signal will result. This project will synthesize the required probes and test them in mock systems before using the probe to detect ROS in Melbourne seawater.
**BCL-X<sub>L</sub> 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-X<sub>L</sub> 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 phenylpyrimidine-oxadiazole 1 (Fig. 2b), 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. 2c). 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.

This project will synthesize novel compounds which will then be tested for activity.

![Figure 2](image)

*Figure 2*: 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.
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:  
http://monash.edu/science/about/schools/chemistry/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). There is massive scope to create your own array of new, porous materials – as demonstrated by our current Honours student.

A Ca-based network containing NDI ligands which form an interpenetrated structure with guest-accessible, chiral channels that displays separation of racemates.

**Amine-Based Porous Materials for CO₂ Capture (with Professor S. 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 CO₂ gas uptake. Traditional solution-phase methods for CO₂ 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 CO₂.

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.

One example of a ligand that is currently used in the project and one of the porous materials – that is 50 % empty space – that this ligand makes.
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:
http://monash.edu/science/about/schools/chemistry/staff/Wilkinson.html

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

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

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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http://monash.edu/science/about/schools/chemistry/staff/bayden.wood.html

**Determination of oocyte competence for IVF treatments using synchrotron FTIR and Raman imaging using living human and mouse oocytes** (with Professor John Carroll)

Polarity and oocyte asymmetry has long been studied, yet established solely in invertebrates such as the *Drosophila* and hitherto not in animals. Thus, we endeavour to correlate a number of molecular imaging based approaches located at Monash University and at the Australian Synchrotron to investigate subcellular constituents, which can offer a novel assessment and insight into the overall morphology and potential polarity of the growing and maturing oocyte. Wood et. al. demonstrated that Synchrotron-FTIR microspectroscopy (*Anal. Chem.* 2008, 80, 9065–9072) is a powerful technique to study biochemical composition of oocytes during maturation. High spatially resolved synchrotron FT-IR and Raman maps of living oocytes provides a way to visualize the macromolecular changes that accompany physiological and biological transformations *in vivo* or *in vitro* systems. By correlating these techniques with other techniques including confocal fluorescence imaging, transmission electron microscopy (TEM), scanning electron microscopy and digital imaging, all of which are available through the Monash Micro Imaging facility, we will provide a multi-modal approach to assess oocyte competence. A key aspect will be the generation of 3D molecular images of human oocytes at different developmental phases including the Germinal Vesicle (GV) and Meiosis II (MII) stage.

![Figure 1. Photomicrograph of GV stage mouse oocyte along with an FTIR image based on the integrated area of the assymetric phosphate stretch form nucleic acids. The nucleoli and polar end are resolved in the image.](image)

**A new modality to diagnose malaria using a portable hand-held Attenuated Total reflectance-Fourier Transform Infrared (ATR-FTIR) system** (with Professor Don McNaughton)

Malaria remains the most deadly parasitic disease on the planet afflicting some 500 million people and resulting in approximately 1 million deaths per annum. We have discovered specific spectroscopic signatures characteristic of the malaria parasite (*Anal Chem* 2009, 81, 2516). We now plan to develop a portable system for the detection and quantification of malaria parasites using the portable hand held Exoscan (See Figure on right). The technique requires a minimal amount of blood, is inexpensive to perform and based on preliminary results using conventional ATR shows extremely high sensitivity. supplied samples through our collaboration with Professor Leann Tilley (University of Melbourne). This project has tremendous commercial potential.
Detection of infrared-biomarkers for the diagnosis and treatment of canine neoplasia (with Professor Don McNaughton)

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. flow cytometry, Polymerize Chain Reaction) 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. Canine neoplasias are not only important within the field of veterinary medicine, but are excellent models for human cancers. In some cases, cancer treatments initially developed for dogs have been carried over to human medicine (melanoma vaccines). The histopathology, behaviour and prognosis is almost identical in dogs. In both human and canine cases of osteosarcoma, sub-clinical metastases are present at the time of diagnosis in the vast majority of cases; biomarkers that could detect the neoplasia before metastasis, are certainly required to improve survival rates. The project will apply FTIR and Raman imaging to find new diagnostic markers for canine cancers.

Monitoring the Molecular Dynamics of Lymphocyte Activation using Synchrotron - FTIR and Raman imaging spectroscopy (with Professor Don McNaughton)

Lymphocytes have a number of properties that enable the study of physiological functions such as division, differentiation, and molecular recognition. A single lymphocyte, for instance, is capable of responding to one or more of a limited number of antigens with a similar molecular structure through the antigen specificity of cell-surface receptors. Antigenic stimulation initiates changes in both the concentration and structure of various macromolecules and thus is ideally suited to spectroscopic analysis and, in particular FT-IR analysis and Raman analysis. We have demonstrated that FTIR spectroscopy can be used to discern activated from non-activated lymphocytes using FTIR spectra of fixed lymphocytes (Applied Spectroscopy, 54, 353-359, 2000). We now plan to investigate functional lymphocytes and monitor the activation process using synchrotron FTIR and Raman imaging. These studies have important implications in assessing organ donor compatibility.

Taxonomic identification of *Eucalyptus* species using a portable hand held device (with Professor Don McNaughton)

*Eucalyptus* sp. are now of great importance for the Australian environment and commercially in other countries, particularly South Africa, China, India and Brazil and to a lesser extent in central and Northern Africa and in Mediterranean countries. Apart from their timber and fibre, which are the basis of huge construction and paper industries, eucalypts are also notable for their oils, use in lowering water tables, horticulture, shade and largely for the bark features and colourful flowers in many species. Many *Eucalyptus* species can be very difficult to characterize in the field without sophisticated Polymerize Chain Reaction technology to investigate genetic sequences. The cuticle of certain eucalypts has been shown to possess a complex and species-specific ornamentation so distinctive that its features can be regarded as diagnostic. We hypothesize that the chemical constitution of the cuticle could be diagnostically useful in distinguishing eucalypts and propose using the Exoscan to test this hypothesis within the field.
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More information on my research can be seen at: www.chem.monash.edu.au/staff/zhang

**Synthesis of new molecular and nanocomposite catalysts and their applications in green chemistry** (with Professor Alan Bond at the School of Chemistry and academic researchers at the University of Melbourne and CSIRO. 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 (CO₂) 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 molecular and nanocatalysts will be synthesized for the electrocatalytic/ photoelectrocatalytic reduction of CO₂ in suitable reaction media at room temperature. Highly sophisticated voltammetric techniques and the corresponding quantitative theories developed at Monash Electrochemistry Group will be employed for sample characterization and better understanding of the fundamental processes occurring during electrocatalytic reactions. Students will also have a chance to have hand on experience on a range of contemporary analytical Instrumentations which are available at Monash University, Melbourne 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 Professor Steven Langford and Professor 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

I also have joint projects with Dr Andy Ohlin and Dr Kei Sato. Please refer to their sections for details.
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**Ordered inorganic mesoporous materials for the architecture of new generation fuel cells** (with Professor Doug Macfarlane)

Today's consumers of portable electronics consumers are demanding devices that not only deliver more power but also are good for the environment. Due to such advantages as high energy-conversion efficiency, easy storage of the liquid fuel, ambient temperature operation, and simple construction, the direct alcohol fuel cell (DAFC) has received much attention as a leading candidate for the portable power of the future. Alcohol (methanol or ethanol) is fed directly into the fuel cell, without any previous chemical modification or purification and it is oxidized at the anode while oxygen is reduced at the cathode. In addition, DAFCs are environment-friendly and can be recharged instantly. The aim of the proposed project is to design and develop novel classes of ordered mesoporous materials with fully controlled geometry and structure and fabricate direct alcohol fuel cells.

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

\[ 6\text{H}^+ + \frac{3}{2}\text{O}_2 + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \]