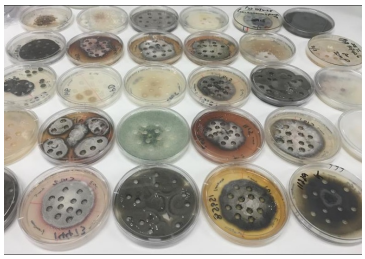
THE UNIVERSITY OF AUCKLAND
Te Whare Wānanga o Tāmaki Makaurau
NEW ZEALAND

School of Chemical Sciences

SUMMER RESEARCH PROJECTS 2017-2018



School of Chemical Sciences Projects
(abstracts below)

A/Prof David Barker Projects d.barker@auckland.ac.nz	Synthesis of biologically active lignan natural products
	Synthesis of Novel inhibitors of Phospholipase C, an enzyme involved in cancer cell proliferation
	Exploring the effect of fluorination on Claisen rearrangement reactions
	Understanding the biogenesis of H2S in yeast and its role cell signalling
	Synthesis of novel polymeric materials as surface active antimicrobial agents
	Synthesis of novel polymeric materials for modern electronic materials
Distinguished Prof Margaret Brimble Research Group Projects m.brimble@auckland.ac.nz	Total Synthesis and Medicinal Chemistry: Spirocyclic Imine Natural Products
	New Chemical Reactions: Synthetic Applications of Vinyl Azide and Vinyl Amides
	Drug Discovery: New Antibiotics Based on Novel Aminoacid Components
	Natural Product Synthesis: Asymmetric Synthesis of Spiroketals
	Synthesis of New Generation Lipopeptide-based Antibiotics
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	Development of Antimicrobial Peptides in the Fight Against Bacterial Resistance
	Synthesis of Amylin Mimics as a Treatment for Diabetes
	The Impact of AGEs in Alzheimer's Disease
	Chemical Synthesis of Prostate Cancer Cell Growth Inhibitors Leucinostatins
	Chemical Synthesis of a Conotoxin Derived from the Venom of Cone Snails
	Synthesis of Pseudoxylallemycins, Antimicrobial Cyclic Tetrapeptides
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Prof Penny Brothers Projects p.brothers@auckland.ac.nz	Lighting up sugars – fluorescent probes for mono-saccharides
	Lighting up sugars – fluorescent probes for poly-saccharides
	Porphyrin compounds for dye sensitised solar cells
	Porphyrin compounds for new functional materials
	Cobalt complexes for catalytic hydrogen production
A/Prof Brent Copp Projects b.copp@auckland.ac.nz	Restoring the activity of old antibiotics
	New Zealand fungi as sources of new antibiotics

Prof Christian Hartinger Projects c.hartinger@auckland.ac.nz	Bioorganometallic Anticancer Chemotherapeutics: Preparation of Metal Complexes with Bioactive Ligands
	Design of Multimodal Organometallic Anticancer Agents
	Design and Applications of Organometallic Complexes for Catalysis
	Bioanalytical Mode-of-Action Studies of Metal-based Anticancer Agents
Dr Paul Hume Projects p.hume@auckland.ac.nz	Zwitterionic Materials for Enhanced Molecular Self-Assembly in Organic Solar Cells
Prof Paul Kilmartin Projects p.kilmartin@auckland.ac.nz	Characterisation of beverage antioxidants using cyclic voltammetry
	Localised interaction of PEDOT electrodes with antioxidants using Scanning Electrochemical Microscopy (SECM)
Dr Erin Leitao Projects erin.leitao@auckland.ac.nz	Using catalysis to create new bioerodible materials useful in the construction of synthetic bone
	Understanding the mechanism of copper-catalysed cross-coupling with main-group substrates
	Catalytic routes to robust polysilanes
Dr Ivanhoe Leung Projects i.leung@auckland.ac.nz	Development of novel inhibitors for *Mycobacterium tuberculosis* isocitrate lyase
	Recombinant protein expression and purification

	Mechanistic and mutagenesis studies of grape (*Vitis vinifera*) polyphenol oxidase
A/Prof Gordon Miskelly Projects g.miskelly@auckland.ac.nz	Behaviour of fingermarks on ice
	Hyperspectral imaging in chemical and forensic analysis
A/Prof Siew-Young Quek Projects sy.quek@auckland.ac.nz	The stability of microencapsulated cranberry powder
Dr Jóhannes Reynisson Projects j.reynisson@auckland.ac.nz	Correlation between predicted and measured hydrogen bonding energies in model systems
	The redox potentials of pro-drugs activated with bio-oxidation/reduction as calculated with DFT
	The physicochemical parameters of veterinary drugs. A comparison study
Dr Viji Sarojini Projects v.sarojini@auckland.ac.nz	Lipopeptides as Antibacterial Coatings for Biofilm Eradication
	Antifreeze Peptides for Preserving Texture in Frozen Foods
	Cell Penetrating Peptide Nanoparticles for Drug Delivery
	Antimicrobial Peptides against Food Spoiling Psychrophiles
	De novo Designed Models of Protein β-sheets

	New Enzymes for Water Treatment
	Anti-Biofilm Peptide-Polymers for Water Disinfection
A/Prof Jonathan Sperry Projects j.sperry@auckland.ac.nz	Novel Synthetic Methods for Indole Construction
	Sustainable Medicinal Chemistry with Biomass-Derived Building Blocks
	New Chemical Technologies for the Depolymerisation of Lignin
	Synthesis of Small Molecules that Influence PSA-NCAM: Potential Therapeutics for the Prevention of Glioblastoma Metastasis
Prof Jadranka Travas-Sejdic Projects j.travas-sejdic@auckland.ac.nz	Atomic force microscopy on polymers
	Electrospinning conducting elastomers
Dr Geoff Wilmott Projects g.willmott@auckland.ac.nz	Surfaces for Dynamic Microfluidics
Prof L. James Wright Projects lj.wright@auckland.ac.nz	Metallabenzenes as building blocks for new materials
	Water purification by catalytic oxidation of pollutants
	CO-Releasing Molecules with Targeted Pharmacological Activity

Synthesis of biologically active lignan natural products

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Lignans are a class of compound which has become the a target of particular interest to researchers, owing to their numerous biological activities including anti-cancer and cytotoxic properties and have also shown an array of pharmacological activities, including antifungal, antibacterial, antioxidant and anti-proliferative properties. In this project we will explore our recently developed methods to prepare a range of classes of lignan natural products using a common, easily made intermediate. This compound can be converted to both THF lignans and also aryl-tetralin lignans, both classes have highly bioactive members including clinically used drug. The student undertaking this project will be involved in organic synthesis, purification and compound characterisation (NMR, MS, IR, etc). They should have a reasonable knowledge of synthetic chemistry.

Synthesis of Novel inhibitors of Phospholipase C, an enzyme involved in cancer cell proliferation

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Phospholipase C is a promising biological target for anticancer drug therapy with compounds binding to PLC showing marked growth inhibition of haematological tumour cells. We have recently discovered a class of compounds which are potent inhibitors of cell growth. Morphology and motility assays using triple negative breast cancer cell lines lead to the conclusion that PLC is the most probable bio-molecular target of these compounds however other important targets may be effected. The student working in this project will be involved in the design (computation modelling), synthesis and biological testing of novel compounds to treat cancer. Students with an interest in organic or medicinal chemistry are encouraged to apply.

Exploring the effect of fluorination on Claisen rearrangement reactions

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The Acyl-Claisen rearrangement is a modern derivative of a classical organic chemistry reaction and allows multifunctional compounds to be prepared which we have found are extremely useful for the synthesis of complex biologically active compounds. In this project we will further explore the use of fluorinated materials in this reaction and discover conditions that allow a variety of substrates to be employed. This will then allow access to a range of poly-functional fluorinated compounds that are otherwise difficult to obtain.

Fluorinated compounds are of considerable interest in drug-like molecules and in amino-acids/peptides for the interesting way they effect both the shape and electronic properties of the molecules. The student undertaking this project will be involved in organic synthesis, purification and compound characterisation (NMR, MS, IR, etc). They should have a reasonable knowledge of synthetic chemistry.

Understanding the biogenesis of H2S in yeast and its role cell signalling

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There is growing recognition that H2S is a "gasotransmitter'' that plays critical roles in cellular signalling and hormonal regulation. In humans, H2S has come under intense recent scrutiny because of its importance in cardiovascular diseases, cellular energetics and apoptosis. Since gaseous transmitters diffuse rapidly and with fine temporal control, understanding their modes and sites of synthesis is critical to understanding their biology. Several enzymes produce H2S, but their roles and relative importance in H2S signalling are not yet clear. In this project students will work on the synthesis of novel H2S donors. These molecules are synthetic complexes that break down under cellular conditions to product H2S and are required to study the effect of H2S in the inter-species signaling. The student undertaking this project will be involved in organic synthesis, purification and compound characterisation (NMR, MS, IR, etc) and also complex analytical techniques such as GCMS and LCMS and they should have a reasonable knowledge of synthetic and/or analytical chemistry.

Synthesis of novel polymeric materials as surface active antimicrobial agents

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Prof Jadranka Travas-Sejdic
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Due to the increase in bacterial resistance there is a need to develop new antibacterial agents, in particular in a hospital and medical environment. In this project we will synthesize novel fluorescent antimicrobial polymers which not only kill bacteria upon contact but allow visualisation of the bacterial killing. The polymers will be designed so they can be used in a either a solution to be applied where desired or could be attached permanently to a surface to give an antibacterial surface. This project is conducted in collaboration with Prof Jadranka Travas-Sejdic. The student undertaking this project will be involved in organic synthesis, purification and compound characterisation (NMR, MS, IR, etc). They should have a reasonable knowledge of synthetic chemistry.

Synthesis of novel polymeric materials for modern electronic materials

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In this project the synthesis of novel polymeric materials will be undertaken with the prepared materials having the unique ability to not only conduct electricity but to also be adhesive and self-healing. The concept is that through appropriate design, materials can be made that are flexible, stretchy but also conducting and would allow for the generation of a new generation of conducting plastics for a wide range of applications, such as optoelectronics, bio-integrated electronic devices and conducting skin and soft robotics. This project is conducted in collaboration with Prof Jadranka Travas-Sejdic. The student undertaking this project will be involved in organic and polymer synthesis, purification and compound characterisation (NMR, Mass, IR, etc) as well as wide range of materials spectroscopy (AFM, SEM XPS etc). They should have an interest in synthetic and/or polymer chemistry.

Total Synthesis and Medicinal Chemistry: Spirocyclic Imine Natural Products

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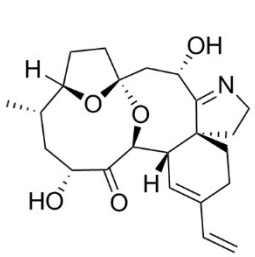
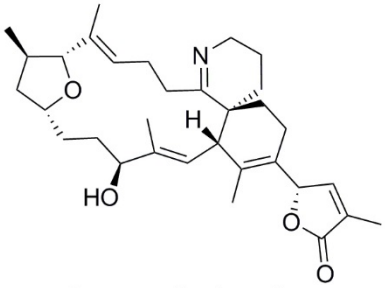


Portimine



Gymnodimine A

Shellfish toxins produced by dinoflagellates in during algal blooms such as portimine and gymnodimine are a significant risk to human health – but also provide a stern challenge for existing synthetic methods, and inspirational leads for medicinal chemistry and drug development. Portimine exhibits promising selective anti-cancer activity and apoptosis induction, and gymnodimine is an extremely selective ligand for the nicotinic acetylcholine receptors important in nerve signal transduction. Our group has a strong ongoing interest in the total synthesis of these complex and highly bioactive molecules, and revealing their potential use in medicinal chemistry through structure-activity studies.

Working in this area will give new students a superb opportunity to be involved in the exciting challenge of natural product synthesis, and gain an insight into the tactics and techniques of complex organic chemistry. Projects currently available in this specific area include; stereoselective assembly of key spirocyclic imine natural product fragments, development of new methods to prepare challenging chemical structures, and determination of structure-activity relationships in partnership with our biochemistry collaborators.

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New Chemical Reactions: Synthetic Applications of Vinyl Azide and Vinyl Amides

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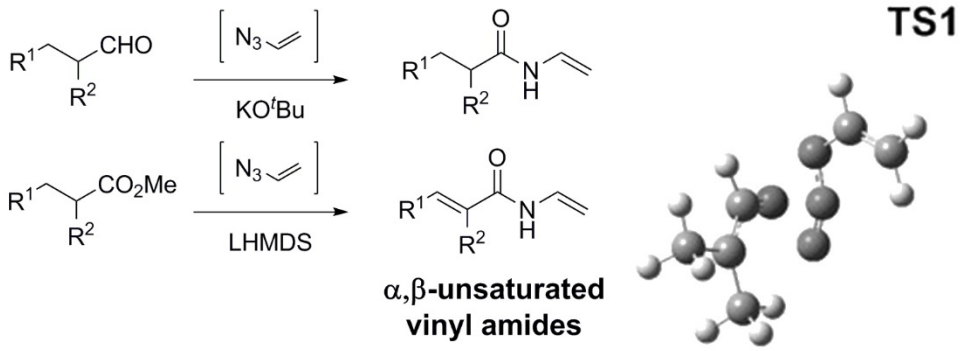
The discovery and development of new reactions offers opportunities to improve synthetic routes to important materials, readily and selectively access previously challenging structures and improve our fundamental understanding of chemical processes. Recently, our group uncovered an unexpected reaction to form alpha,beta-unsaturated vinyl amides directly from esters. Our investigations revealed that the reaction likely involves an unusual [3+2] cylcloaddition of an ester or aldehyde enolate, with

in situ generated vinyl azide, a little-used reagent with an intriguing history dating back to original work in 1910.



We are keenly pursuing the possibilities opened up by this new reactivity; for rapid access to previously hard-to-access vinyl amides (versatile synthetic intermediates and useful industrial polymer feedstocks) and synthesis based on them; to explore the mechanistic basis of their reactivity through experiment and calculation (e.g. transition state TS1); and finally to assess the potential of vinyl azide itself in organic synthesis. This project offers an unusual and fast-moving chance to discover new areas of chemistry, while expanding your synthesis and lateral thinking skills.

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Drug Discovery: New Antibiotics Based on Novel Aminoacid Components

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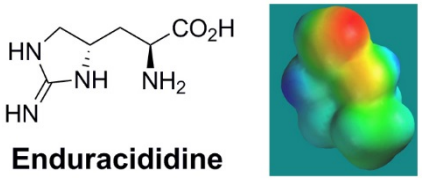

Growing incidence of antimicrobial resistance to clinically used antibiotic drugs is an immediate global health concern, as recently highlighted by the World Health Organisation (WHO), US and NZ governments. Due to the low numbers of new pharma drug candidates currently entering the development pipeline, academia and small biotech firms have an important role to play in generating novel compounds to address the resistance problem. Teixobactin, a complex antimicrobial peptide recently isolated from a culture of soil bacteria, demonstrates not only extremely potent activity against clinically-relevant resistant strains of MRSA, vancomycin-resistant Enterococci (VRE), M. tuberculosis (Mtb) and C. difficile, but crucially a very low incidence of acquired resistance.

The rare aminoacid enduracididine (End) is critical to the activity of teixobactin, but has proven surprisingly challenging to synthesise. Work on this project offers the chance to learn important synthesis skills in a drug discovery context, on a problem of genuine global relevance. The development of a robust and efficient route to End itself and the preparation of new active analogues to support medicinal chemistry studies will be the initial project goals, with the eventual aim of

identification and synthesis of new antimicrobial peptide drug candidates, in collaboration with the group's SBS-based peptide unit.

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Natural Product Synthesis: Asymmetric Synthesis of Spiroketals

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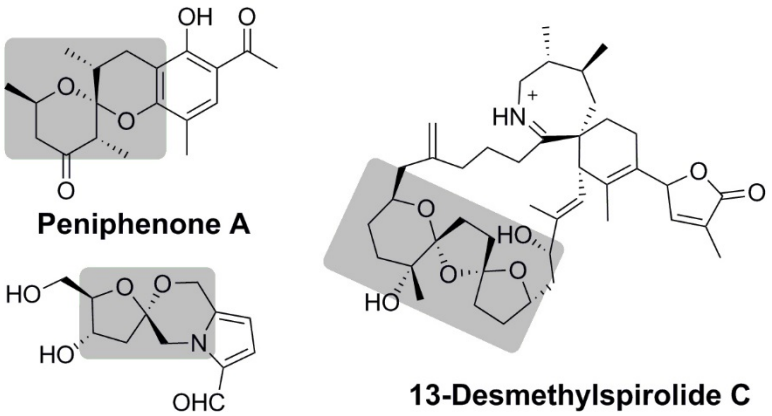

Synthesis of spiroketals and spiroketal-containing natural products is a longstanding interest of our group. These molecular scaffolds, consisting of two (or sometimes even three) rings joined at a quaternary carbon with two bonds to oxygen, are found in a wide range of natural products that demonstrate interesting bioactivity. Some examples of our current and previous targets are shown (spiroketals highlighted in grey).

This research area offers a great opportunity to apply your organic chemistry background to natural product synthesis, building on our group's particular expertise in spiroketals. Projects will based on stereoselective multistep organic synthesis, aiming to successfully prepare structures found in recently-isolated natural products. There will be a chance to learn a wide variety of classic and state-of-the-art chemistry techniques for asymmetric synthesis including catalysis, pericyclic reactions, aldol reactions and organometallic additions.

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Synthesis of New Generation Lipopeptide-based Antibiotics

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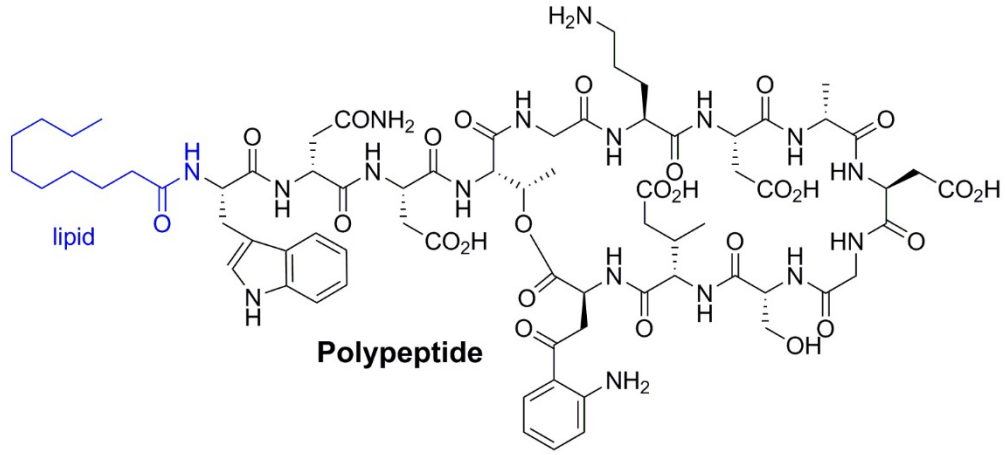
Antibiotic resistance has been recognised by the WHO as one of the greatest threats to humanity and infectious diseases rank as the second most common cause of death worldwide. This is further compounded by the observation that development of new structural classes of antibiotics has all but ceased in the past 40 years.



An emerging subset of peptide based antibiotics e.g. daptomycin are cyclic peptides containing a lipid or fatty acid. They have been shown to be clinically relevant and are used as the "last line of defence" against otherwise untreatable bacterial infections. The challenge remains, however, to efficiently produce new antibiotics based on a cyclic peptide scaffold incorporating the crucial lipid motif.

Using our newly devised method of installing a lipid onto a peptide (a thiol-ene reaction), this projects aims to exploit and develop this chemistry to generate a chemical library of peptide based antibiotics, which will undergo biological testing against the most antibiotic resistant strains of bacteria.

Successful candidates will be using organic synthesis techniques and modern methods of solid phase peptide synthesis.

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Synthesis of the Novel Macrocyclic Peptide, Streptide

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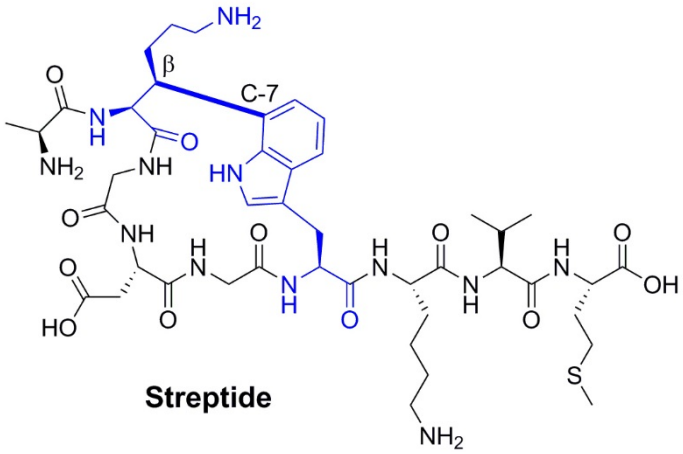
Quorum sensing is a system of intercellular communication by which some species of pathogenic bacteria coordinate the regulation of gene expression and production of virulence factors in order to have maximum impact on their environment. As a result, quorum sensing has significant implications in the pathogenicity of disease-causing bacteria. Understanding the transcription products involved in quorum sensing systems provides insight into the regulation of these systems and may help identify potential biological targets for the development of novel antibiotic compounds that inhibit quorum sensing.



Streptococcal bacteria use peptide signals as a means of intraspecies communication. These peptides can contain unusual post-translational modifications, providing opportunities for expanding our understanding of nature's chemical and biosynthetic repertoires. Streptide is a novel macrocyclic peptide produced by Streptococcus thermophilus, a non-pathogenic streptococcal model strain that is used in the fermentation of dairy products. Although it does not express the virulence factors of its pathogenic relatives (which include Streptococcus mitis, Streptococcus pyogenes and Streptococcus pneumoniae), it does harbour a new, recently identified quorum sensing system common to many streptococci, including pathogenic strains.

Streptide contains an unprecedented tryptophan-lysine cross-link (C-7 to beta) in the macrocycle. In combination with solid phase peptide synthesis, C-H activation will be used to install the tryptophan-lysine cross-link and synthesise the unnatural amino acid (blue) required to complete an initial total synthesis of streptide.

A successful synthesis will allow evaluation of the biological activity of streptide and will provide the basis for future syntheses of related cross-link-containing macrocyclic peptides.

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Development of Antimicrobial Peptides in the Fight Against Bacterial Resistance

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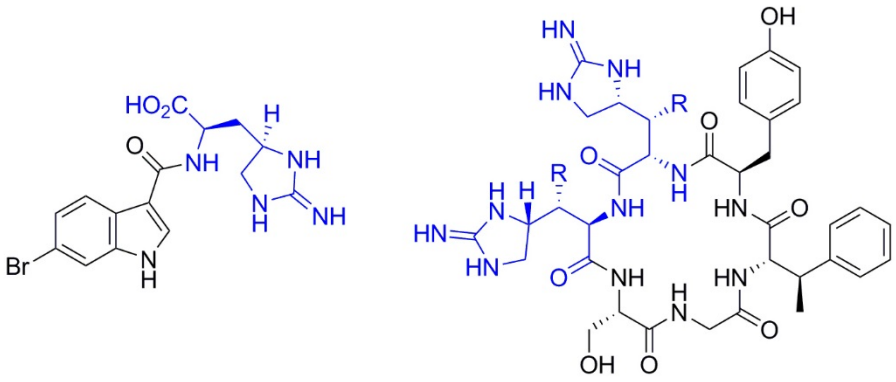
The emergence and spread of multi-drug-resistant bacteria is becoming a great threat to the health of humankind. The rate of bacteria developing resistance to both frontline and 'last line of defence' antibiotics is currently greater than the introduction of new compounds into clinical practice. This poses a severe problem as simple routine medical procedures will become life threatening as any resulting bacterial infection will not be easily and effectively treated.



Ascidian metabolite **Mannopeptimycin**

Naturally-occurring antimicrobial peptides (AMPs) are the tools by which many living organisms employ to defend themselves against bacterial attack. These unique compounds therefore show great potential as new source of antibiotics.

The ascidian metabolite and mannopeptimycin have been show to possess antimicrobial activity and contain the rare cyclic amino acid enduracididine (highlighted in blue).

This project will involve two aspects of modern synthetic chemistry. Firstly, an organic synthesis of enduracididine and secondly, solid phase peptide chemistry to incorporate End into synthetic polypeptides. A successful synthesis of enduracididine will not only allow access to the above antimicrobial peptides and therefore the development of more potent analogues though SAR studies, but provide the basis for investigation of other peptides containing this intriguing amino acid e.g. teixobactin.

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Synthesis of Amylin Mimics as a Treatment for Diabetes

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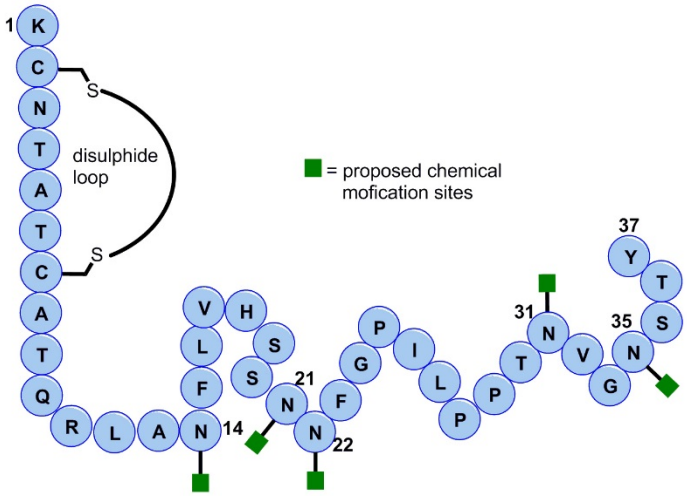

Summer Project Information, Brimble Research Group, School of Chemical Sciences

Diabetes Mellitus (DM) is a vast worldwide medical problem. The associated medical complications lead to heart disease, stroke, renal failure, premature blindness, amputation and significant mortality rates.

Existing therapies revolve around maintaining glucose at an appropriate level by administration of pramlitide, a 37 amino acid residue polypeptide a structurally related but non-toxic analogue of Amylin. However, pramlitide therapy suffers from several shortcomings such as low bio-availability and a half-life of just 48 mins thus necessitating a challenging 3 times daily injection.

Lipidation of polypeptides or glycosylation of polypeptides is known to increase both circulatory half-life and bio-availability whilst maintaining biological effects. Using click chemistry or thiol-ene chemistry, this research project aims to install lipids or sugars in a chemoselective manner on specific amino acid residues thereby synthesising modified pramlitide molecules that will be submitted to both biological evaluation (Prof. Debbie Hay, SBS) and estimation of half-life in the body by enzymatic hydrolysis.

Successful candidates will employ organic synthesis techniques to access suitable glycosylated amino acids, solid phase peptide synthesis to prepare polypeptides and be exposed to biological testing techniques.

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The Impact of AGEs in Alzheimer's Disease

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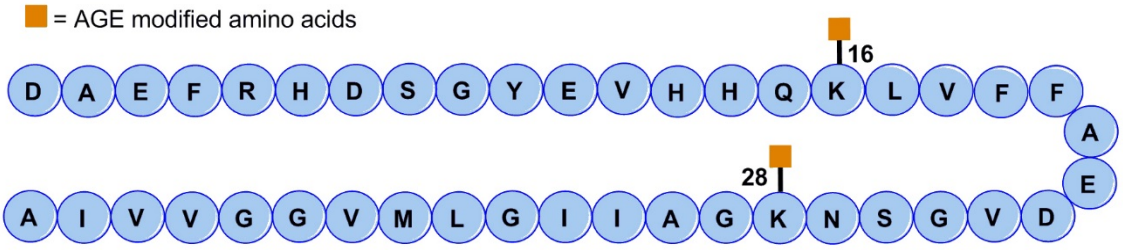

Alzheimer's disease (AD) is a complex neurodegenerative disorder that results in progressive cognitive impairment, loss of memory and changes in behaviour. In 2011, 34 million people worldwide were diagnosed with AD, and it is estimated that this figure will triple by 2050 due to an increasing ageing population. Despite vast research spanning more than a century, current treatments for AD are still limited to modest symptomatic relief and the precise causes of AD remain largely unknown.

Recently, new evidence has suggested that beta-amyloid (A-beta) peptides (a hallmark of AD) that have been irreversibly modified by sugar derivatives known as advanced glycation end products (AGEs) are more pathogenic than A-beta itself. However, the A-beta-AGE peptides used in these studies were prepared by the non-specific incubation of A-beta in glucose; this results in the formation of a complex mixture of A-beta-AGE peptides. Thus, the precise impact of individual AGEs on the biophysical properties of A-beta remains to be evaluated.

Summer Project Information, Brimble Research Group, School of Chemical Sciences

This project aims to prepare a small library of A-beta-AGE peptides, which will then undergo biological testing by Associate Professor Nigel Birch (SBS) and Professor Michael Dragunow (FMHS). Successful candidates will employ organic synthesis techniques to prepare AGE building blocks followed by incorporation of the AGE building blocks into the A-beta peptide using solid phase peptide synthesis.

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Chemical Synthesis of Prostate Cancer Cell Growth Inhibitors Leucinostatins

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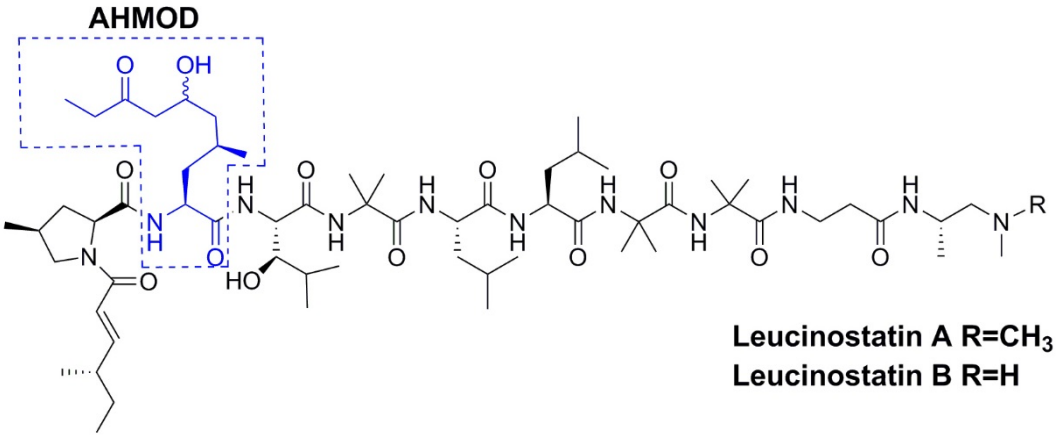

Leucinostatins are naturally occurring peptides which were isolated from Penicillium lilacinum almost 40 years ago. Twenty-four different structures have been described in the leucinostatin family, with leucinostatins A and B significantly suppressing prostate cancer growth in a coculture system in which prostate stromal cells stimulated the growth of DU-145 human prostate cancer cells through insulin-like growth factor-I.

In order to execute the total synthesis of leucinostatins A and B, synthesis of the seven unnatural amino acid building blocks namely: (2*S*)-*N*',*N*'-dimethylpropane-1,2-diamine (DMPD), (*S*)-*N*'-methylpropane-1,2-diamine (MPD), *beta*-hydroxyleucine (*beta*-HyLeu), 4-methyl-L-proline (MePro), (4*S*,2*E*)-4-methylhex-2-enoic acid (MeHA), (2*S*,4*S*,6*S*)-AHMOD and (2*S*,4*S*,6*R*)-AHMOD is required. Site-specific individual incorporation of a (2*S*,4*S*,6*S*)-AHMOD or (2*S*,4*S*,6*R*)-AHMOD residue into the peptide framework of leucinostatin is also required to determine the absolute configuration at C-6 in the AHMOD residue.

Solid-phase peptide synthesis (SPPS) techniques will be used for peptide elongation to avoid tedious purification of the intermediates, thus expediting the assembly of the target nonapeptide.

This research project aims to establish a comprehensive structure–activity relationship of leucinostatins A and B in order to search for analogues with improved anti-tumor properties.

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Chemical Synthesis of a Conotoxin Derived from the Venom of Cone Snails

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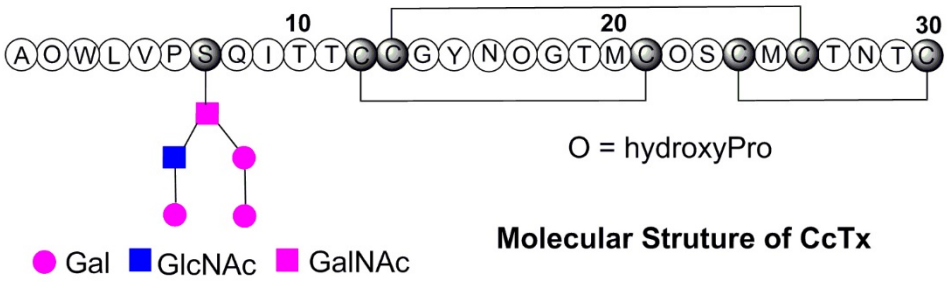

Cone snails have evolved a venomous harpoon able to paralyse prey with an arsenal of toxic compounds, such as conotoxins, which show great promise in the treatment of conditions such as pain and neuromuscular disorders. κA-conotoxins are a major component of the venom of several species of fish-hunting cone snail, but as a class of compounds have been less well studied due to their molecular complexity and post-translational modifications.

CcTx is a 30 residue glycopeptide that contains an intricate serine-linked pentasaccaride, 3 intramolecular disulphide bonds, several hydroxylated proline residues and a C-terminal alpha helix spanning residues 23Ser-27Thr. The unique pentasaccaride moiety, which contains several rare and unnatural L-sugars, probably plays a key role in its bioactivity.

Using chemical synthesis techniques this project will embark on a total synthesis of CcTx using glycosylation and peptide chemistry to assemble from individual amino acids, the fully functional molecule. Candidates will become well versed in the modern methods of glycopeptide chemistry including exposure to advanced biophysical techniques such as HPLC and mass spectrometry.

http://brimble.chem.auckland.ac.nz/?q=research

Synthesis of Pseudoxylallemycins, Antimicrobial Cyclic Tetrapeptides

Distinguished Professor Margaret Brimble, Dr Harveen Kaur, Dr Dan Furkert
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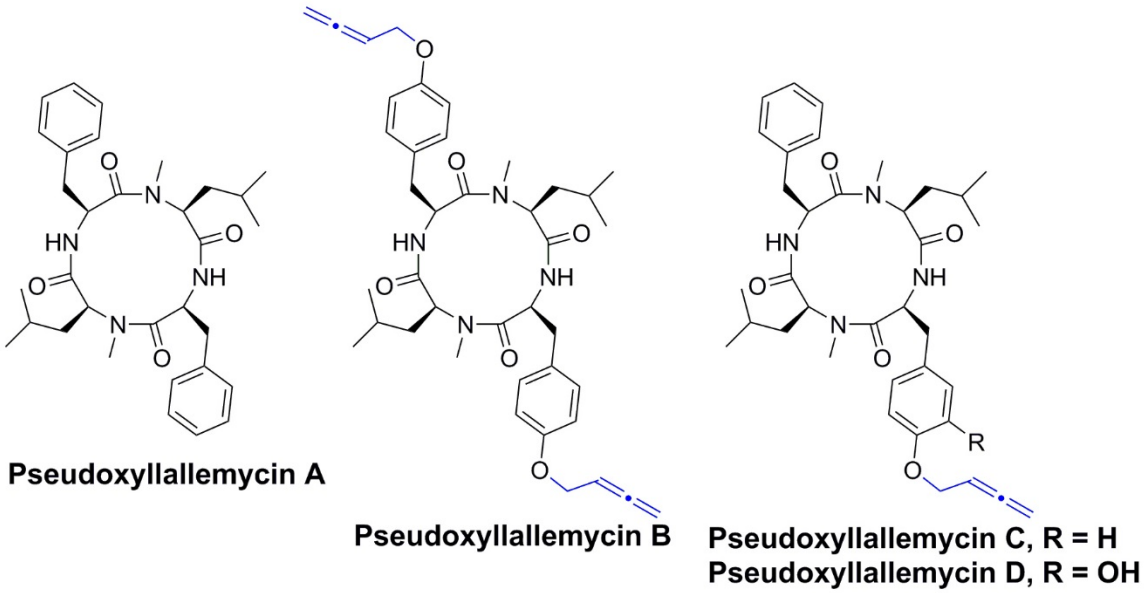
Phone: 09-9238259,
Email: m.brimble@auckland.ac.nz

Multidrug antibiotic resistance poses an increasingly urgent threat to human health. Amongst antibiotic resistant species, Gram-negative bacteria in particular have become resistant to almost all available treatments. Whilst a number of antibiotics are currently being developed to target Gram-positive infections, only few are in progress for Gram-negative infections.



Recently, a family of four cyclic tetrapeptides, namely pseudoxylallemycins A-D, isolated from the termite-associated fungus Pseudoxylaria sp. X802 were found to exhibit Gram-negative antimicrobial activity (MICs of 12.5-25.0 µg/mL), cytotoxicity (HeLa cells, CC50 10.3-49.5 µg/mL) and antiproliferative activity (HUVEC cells, GI50 4.3-33.8 µg/mL; K-562 cells, GI50 4.2-42.8 µg/mL).

Pseudoxylallemycins B-D contain unique allene moieties (highlighted in blue), which rarely occur in natural products. Using a combination of organic and peptide chemistry, this project aims to synthesise the natural products pseudoxylallemycins A-D and structurally related analogues, which will then be evaluated for antimicrobial activity in collaboration with Professor Greg Cook (Uni of Otago).

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TLR2 Activation: Modulating the Activity of Lipopeptide Constructs

Professor Margaret Brimble, Dr Geoff Williams, Professor Rod Dunbar (SBS)
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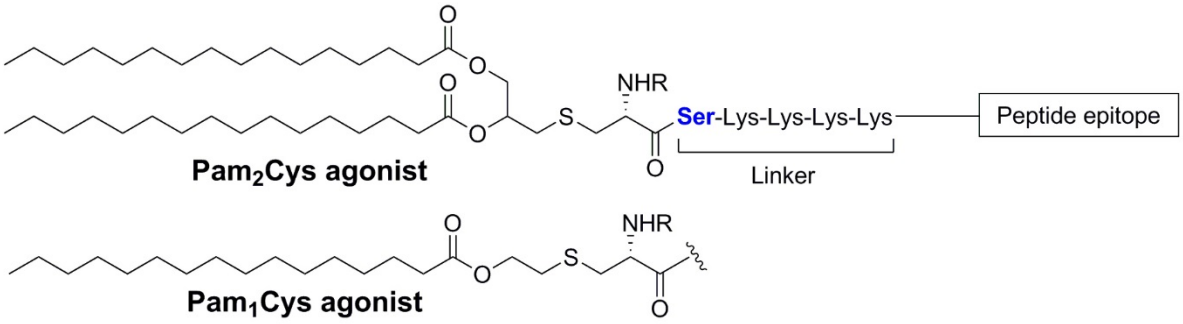
Toll-like receptor 2 (TLR2) is a highly conserved membrane pattern recognition receptor that has evolved to recognize Lipoprotein motifs expressed by foreign pathogens. On binding of an agonist motif the receptor is activated and, after internalisation of the foreign agent, then modulates the production of signalling factors that up-regulate an effective immune response to that pathogen.

It has been shown that activation of TLR2 can be attained with S-(2,3-bispalmitoyloxypropyl)Cysteine-based (Pam2-Cys and Pam-1-Cys) lipid motifs present in the cell wall of Gram-positive bacteria. Thus, by creating a construct in which this lipid is linked to a suitable peptide epitope, the TLR2 receptor can be recruited into producing a highly targeted immune response that can then be directed against cancerous cells within a host.



The linker portion of the lipid-peptide construct epitope has conventionally been Ser-Lys-Lys-Lys-Lys but it is still not clear to what extent TLR2 activation is governed by this sequence. The project aims to investigate this question by exchanging the key Serine residue by other amino acids – both natural and unnatural – to gauge the effect on receptor activation and through this to better modulate the immunogenic response. The relative activity of the library of analogues thus generated will be evaluated in the HEK-blue™ cell assay.

The skills necessary to carry this project out will include some organic synthesis and modern solid-phase peptide synthesis and purification.

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Lighting up sugars – fluorescent probes for mono-saccharides

Prof Penny Brothers, Dr David Ware
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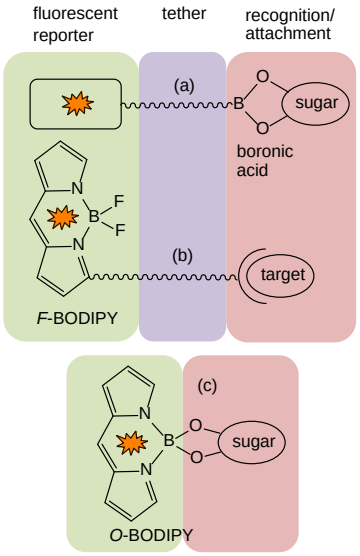
We have developed a method of attaching a fluorescent label directly to glucose. This allows for highly targeted, sensitive, fluorescent labelling of sugars which could be applied to the detection of specific sugar disease markers on cell surfaces, the labelling of saccharide capsules coating pathogenic bacteria, and the determination of polysaccharide fine structure in biology and materials science. The project will involve exploring the chemistry of the fluorescent BODIPY molecule and its chemistry with sugars, *focussing on monosaccharides*.



Activities: chemical synthesis and spectroscopy
Skills: Stage 2 or 3 organic or inorganic chemistry

Lighting up sugars – fluorescent probes for poly-saccharides

Prof Penny Brothers, Dr David Ware
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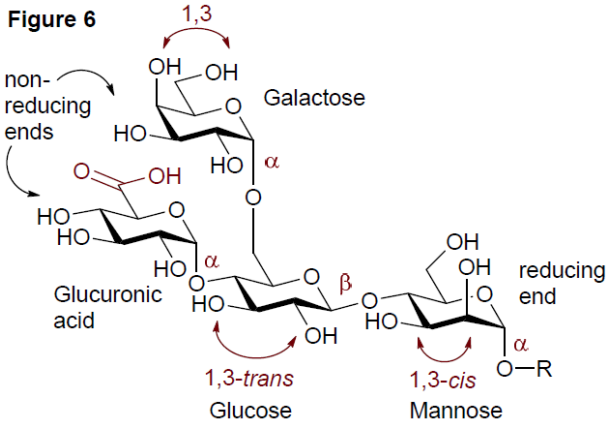
We have developed a method of attaching a fluorescent label directly to glucose. This allows for highly targeted, sensitive, fluorescent labelling of sugars which could be applied to the detection of specific sugar disease markers on cell surfaces, the labelling of saccharide capsules coating pathogenic bacteria, and the determination of polysaccharide fine structure in biology and materials science. The project will involve exploring the chemistry of the fluorescent BODIPY molecule and its chemistry with sugars, *focussing on polysaccharides*.

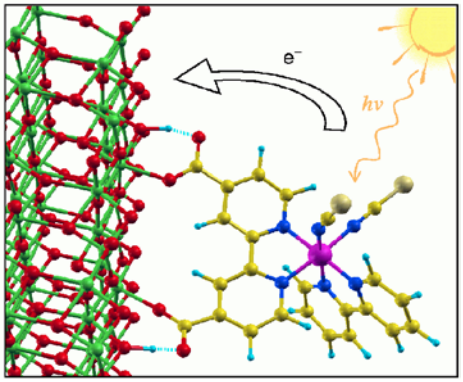


Activities: chemical synthesis and spectroscopy
Skills: Stage 2 or 3 organic or inorganic chemistry

Porphyrin compounds for dye sensitised solar cells

Prof Penny Brothers, Dr Duncan McGillivray
p.brothers@auckland.ac.nz; 09 923 8281; Room 302-1065

Porphyrins are the pigment which gives heme its red colour. These planar, electron-rich molecules are good absorbers of light and can also bond to small gas molecules. They are investigated widely as dyes for solar cells. This project will explore the synthesis of a range of porphyrins designed for these applications.



Activities: chemical synthesis, surface chemistry, spectroscopy, electrochemistry
Skills: Stage 2 or 3 chemistry

Porphyrin compounds for new functional materials

Prof Penny Brothers, Dr David Ware, Prof David Williams
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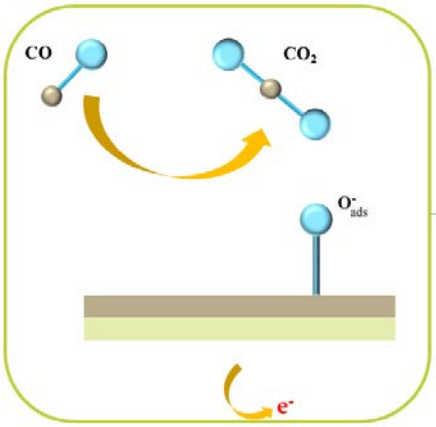
Porphyrins are the pigment which gives heme its red colour. These planar, electron-rich molecules are good absorbers of light and can also bond to small gas molecules. In this project they are investigated as the active site in gas sensors, and for their ability to act as building blocks in new functional electronic materials. This project will explore the synthesis of a range of porphyrins designed for these applications.



Activities: chemical synthesis, surface chemistry, spectroscopy, electrochemistry
Skills: Stage 2 or 3 chemistry

Cobalt complexes for catalytic hydrogen production

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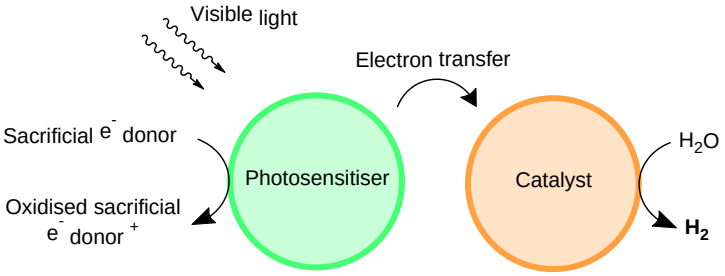
The efficient production of hydrogen from sustainable sources is an important goal in the search for new fuels. We have recently developed a cobalt-BODIPY dye complex which can be used for the photocatalytic production of hydrogen from water. This kind of technology is directed towards the use of sunlight to drive hydrogen production.



Activities: chemical synthesis, laser spectroscopy, electrochemistry
Skills: Stage 2 or 3 chemistry

Restoring the activity of old antibiotics

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Dr Siouxie Wiles
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Antibiotic drug resistance is a rapidly growing problem for global public health. In many cases, current antibiotics simply don't work anymore. We've discovered a new class of molecule that can restore the antibiotic action of drugs against a human pathogenic Gram negative microbe, *Pseudomonas aeruginosa*. Since our initial finding, we've synthesized a lot of analogues, undertaking an extensive structure-activity relationship study, to the point that we now have developed some exceptionally potent analogues. We still don't know exactly why our compounds work though. This summer project is designed to get you into the lab and making novel analogues in this series that can help us understand how these compounds work. The research you undertake in this summer project can be extended into a BSc Hons project, and eventually into a PhD if you're interested.

New Zealand fungi as sources of new antibiotics

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b.copp@auckland.ac.nz

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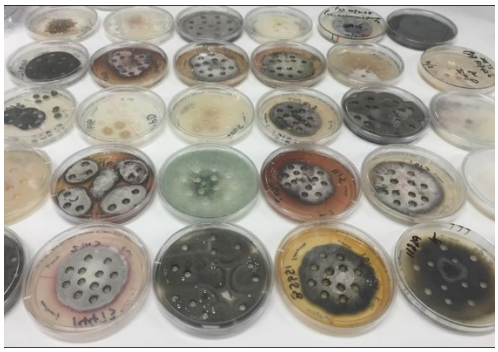

Alexander Fleming's discovery of penicillin, an antibiotic produced by the fungus *Penicillium rubens*, saw the dawn of a golden age for humankind. The routine use of antibiotics has since prevented a great deal of suffering and saved countless lives. Worryingly, that era is now coming to an end whereby antibiotic resistance means that many antibiotics are no longer effective as bacteria have developed the mean to evade and/or destroy these life-saving medicines. We are searching for new antibiotics using a large collection of fungi, most derived from plants and soil from New Zealand and the South Pacific. We are screening this collection to discover new compounds that kill the superbugs causing the greatest clinical threat to New Zealand: *Staphylococcus aureus*, *Escherichia coli* and *Mycobacterium tuberculosis.* This project will have you undertaking metabolomics profiling of antibacterial extracts, using HPLC and NMR to investigate the natural product components. Bioassay-guided fractionation will then be used to purify the active component(s) of each extract – testing of which against our bacteria panel will then reveal if we have something worth pursuing. The research you undertake in this summer project can be extended into a BSc Hons project, and eventually into a PhD if you're interested.

Bioorganometallic Anticancer Chemotherapeutics: Preparation of Metal Complexes with Bioactive Ligands

Prof. Christian Hartinger
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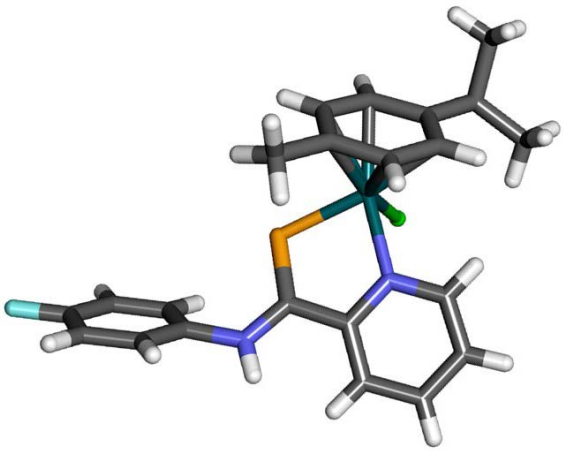
Medicinal bioinorganic chemistry is a relatively new but fervent area of research. It offers possibilities for the design and development of metal-based drugs for specific therapeutic needs that are not readily accessible to organic compounds. Currently, iron, ruthenium and osmium organometallic compounds have become the focus of interest and appear to be promising anticancer drug candidates. Some examples are at an advanced stage of preclinical development. Among the half-sandwich, piano-stool configured organometallic anticancer complexes, two most extensively studied approaches involve the coordination of ethylenediamine (en) and 1,3,5-triaza-7-phosphatricyclo[3.3.1.1] decane (pta) ligands to metal centres. *In vivo* studies on bifunctional RAPTA-C revealed excellent inhibition of metastasis growth. Monofunctional $[Ru(\eta^6\text{-arene})Ru(en)Cl]^+$ type complexes were found to have *in vitro* anticancer activity similar to that of cisplatin, one of the most widely used anticancer drugs in clinics.



Within this project a series of organometallic metal-arene compounds (metal = ruthenium and osmium) will be prepared to feature bioactive ligands. We are currently focusing on *O*,*O*-, *N*,*O*- and *S*,*N*-chelating ligands which are chosen based on their intrinsic biological properties. The compounds that we will prepare in this project, will be evaluated for potential anticancer activity by *in vitro* assays. Experiments on biologically-relevant metabolisation including hydrolysis, interactions with proteins and DNA model nucleobases will be carried out.

The student will be exposed to different levels of the drug development process and will gain extensive training in a range of synthetic procedures (both organic and inorganic synthesis) and separation/purification techniques. The prepared compounds will be characterised with state-of-the-art analytical methods (NMR, IR and UV/vis spectroscopy, electrospray ionisation mass spectrometry and X-ray diffraction analysis).

Design of Multimodal Organometallic Anticancer Agents

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Since the discovery of cisplatin, the design of most metallodrugs has been based on the paradigm that DNA is the target in tumour cells. Such agents however cannot explicitly discriminate between healthy and cancerous cells. More recently this paradigm has shifted and a small body of research has been aimed at developing inhibitors of specific enzymatic targets via organometallic compounds. Late transition metals such as ruthenium and osmium are ideally suited for this purpose. Their (relatively slow) ligand exchange rates and versatile synthetic chemistry can be exploited to construct novel structural scaffolds (e.g. octahedral motifs) that are not generally accessible to purely organic small molecules, which are largely restricted to tetrahedral, planar, or linear geometries. This molecular complexity can be utilized for developing inhibitors of specific enzymatic targets by linking a metallopharmacophore to a ligand or to construct metal complexes that resemble the shape of substrates of such enzymes. In tumours, a number of proteins are upregulated, often to satisfy the increased demand of rapidly dividing cancerous cells for nutrients. These alterations in tumours can be successfully targeted for rational design of anticancer agents with high selectivity. One of such targets are zinc-containing histone deacetylases (HDACs) which are considered important targets for anticancer chemotherapeutics but others will be considered as well. Connecting two or more pharmacophore will result in a compound that can bind to more than one target and thereby provide a means to overcome drug resistance through multi-modal activity.

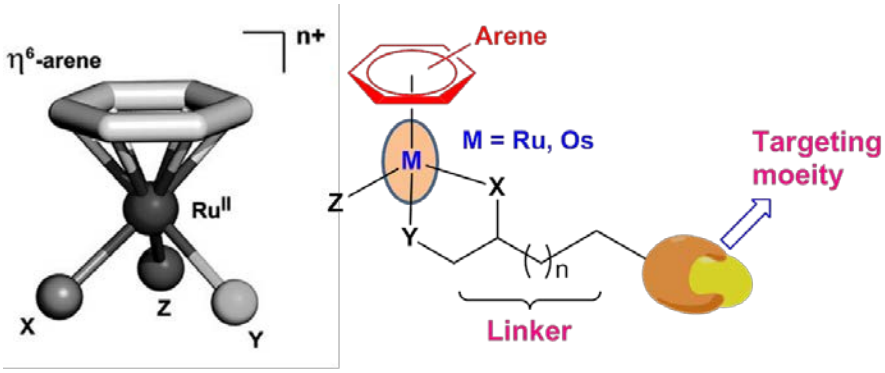

Figure. *General structures of half-sandwich, piano-stool metal(arene) complexes (left) and outline of the design strategy for multimodal organometallic anticancer agents (right).*

The student will be exposed to different levels of the drug development process and will gain extensive training in a range of synthetic procedures (both organic and inorganic synthesis) and separation/purification techniques. The prepared compounds will be characterised with state-of-the-art analytical methods (NMR, IR and UV/vis spectroscopy, electrospray ionisation mass spectrometry and X-ray diffraction analysis).

Design and Applications of Organometallic Complexes for Catalysis

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Prof. James Wright
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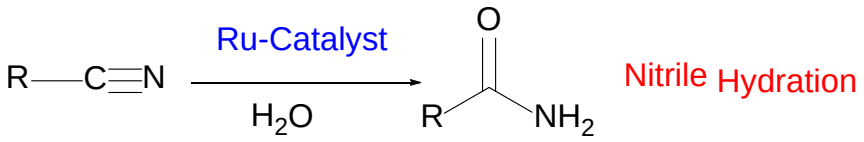
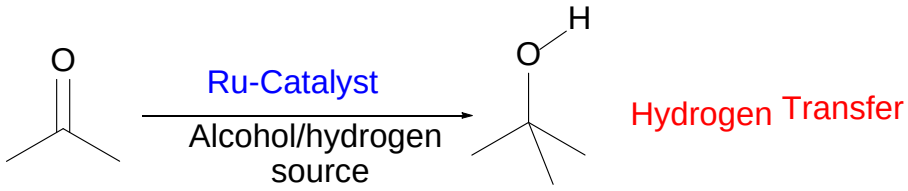
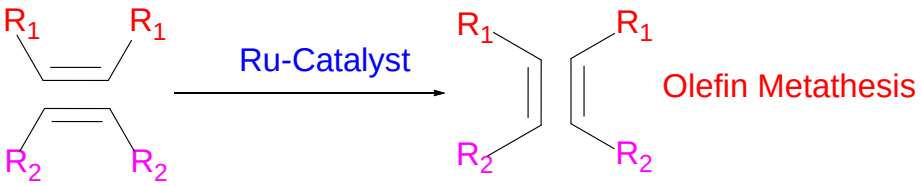
The production of everyday products, such as pharmaceuticals, fertilisers and functional materials, is reliant on efficient chemical transformations to yield high amounts of the desired products at low cost. Catalytic processes are often the only efficient option to prepare certain compounds. In recent years, we have designed a large variety of ruthenium complexes featuring ligands with phosphorus, nitrogen, oxygen and sulphur donor atoms.
In this project we want to explore the use of such ruthenium complexes as catalysts for different reactions. These will range from the hydration of nitriles, transfer hydrogenation of ketones to olefin metathesis. Each of these reactions has a very important role in the preparation of chemicals widely used in industry.







The student will gain extensive training in a range of synthetic procedures (both organic and inorganic synthesis) and analytical methods to characterize compounds and study their catalytic properties (TON, TOF). The methods employed will include NMR, IR and UV/vis spectroscopy, HPLC, GC and electrospray ionisation mass spectrometry.

Bioanalytical Mode-of-Action Studies of Metal-based Anticancer Agents

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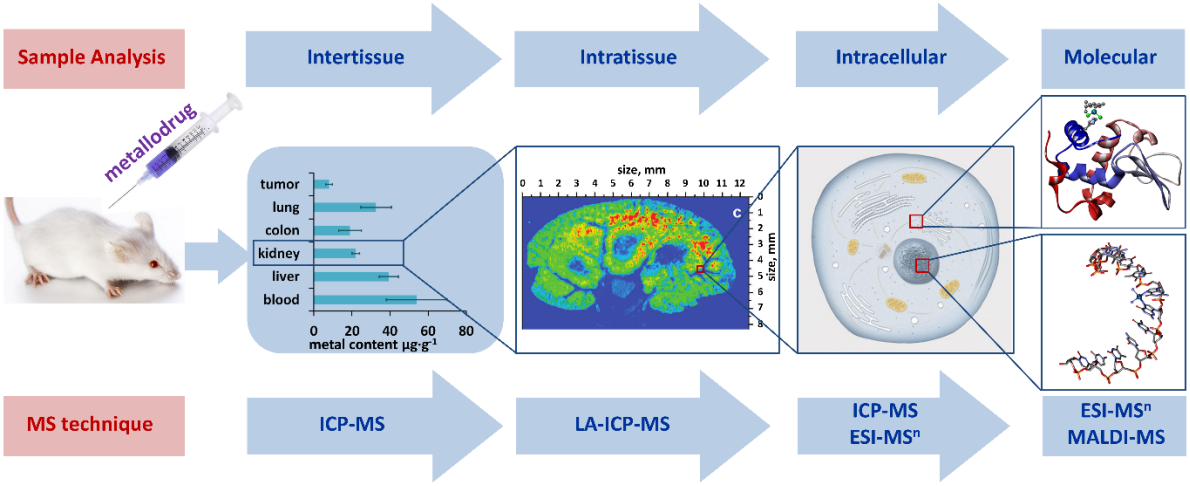
DNA has been identified as the target of Pt-based anticancer agents in tumour cells. However, until anticancer drugs reach DNA, they may interact with many other biological molecules. Therefore, we extensively study the binding of metal-based anticancer agents with amino acids and with proteins. For this purpose, we use different analytical methods which include capillary electrophoresis, gel electrophoresis, X-ray diffraction, high performance liquid chromatography, NMR spectroscopy and mass spectrometry (Figure).



In this project, the student will be learn about different levels of the drug development process and will gain training in analytical methods such as NMR, X-ray diffraction, CE, HPLC and electrospray ionisation mass spectrometry. The project will involve studying the interactions of metal complexes designed as anticancer agents with biological binding partners. Studies with model proteins will be followed by experiments to elucidate the interaction with (serum) proteins. This studies will allow us identifying the influence of different structural components on the reactivity of metal complexes. This is important information to decide which compounds to put forward for further in depth preclinical studies as anticancer agents.

Zwitterionic Materials for Enhanced Molecular Organisation in Organic Solar Cells

Paul Hume, p.hume@auckland.ac.nz

Among the current options available for solar energy production, organic solar cells (OSCs) show considerable potential for development. This is due to their low material costs and compatibility with high-throughput production techniques. **The goal of this work is to prepare novel zwitterionic materials for use in organic solar cells. It is hoped that these materials will lead to improved solar cell performance via supramolecular self-assembly.**

The precise arrangement of molecules in OSCs is a vital factor influencing performance. However at present, the use of intermolecular interactions to enhance performance *via* molecular self-assembly is under-utilised. Aside from π-π stacking of chromophores, current strategies to improve OSC performance targeting self-assembly are mostly limited to hydrogen bonding and dipolar interactions. In particular, the relative positions of π-π stacked molecules has a large effect on charge transport in OSCs. but precise control over the lateral displacement between molecules is difficult to achieve. A novel way to achieve such control would be to "lock" the molecules relative to one another by the introduction of specific interactions acting parallel to the π-π stacking direction. It is hoped that zwitterionic materials would satisfy this requirement, controlling the lateral displacement of the planar aromatic units by local electrostatic forces. **This project will involve the synthesis of novel zwitterionic materials and characterisation of their electrochemical, optical and structural properties.** The compounds investigated will be based on 1,4-diketopyrrolopyrrole (DPP) and thienopyrrole-4,6-dione (TPD). These well-studied chromophores are known to exhibit favourable photo-physical properties and are chemically and thermally stable under the conditions required for solar cell fabrication (Figure 1).

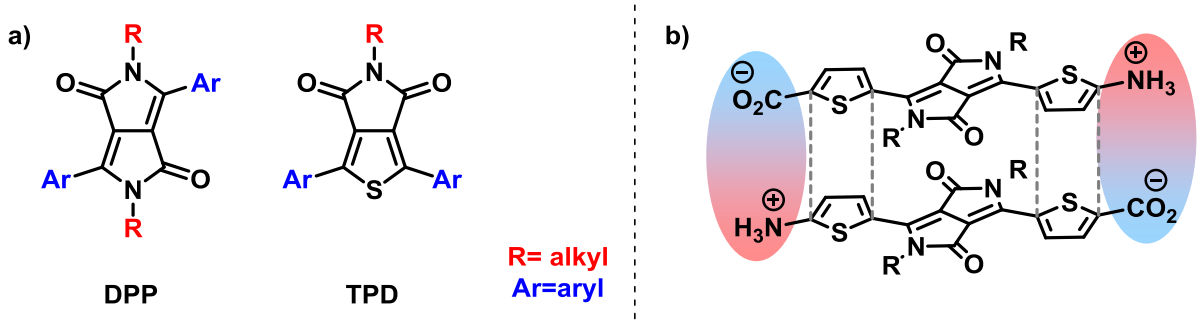


Figure 1. a) Chemical structures of DPP and TPD b) Example of a zwitterionic material based on DPP.

Characterisation of beverage antioxidants using cyclic voltammetry.

Prof. Paul Kilmartin
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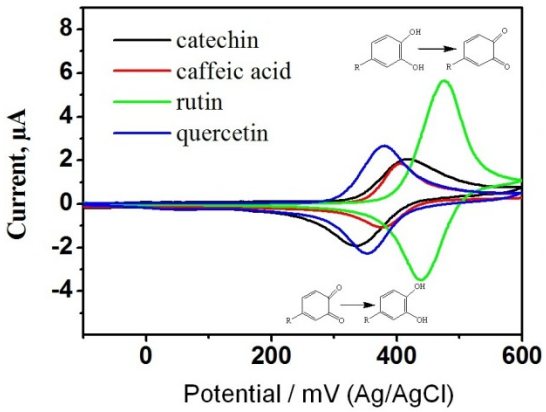
The antioxidants present in beverages can be quantified and information provided about their reducing strength using the electrochemical technique of cyclic voltammetry. This technique has been developed at the University of Auckland to profile wines, fruit juices, teas and coffees, and milk. In this project, the voltammetry procedure will be applied to the antioxidants present in a series of alcoholic beverages, including beer and fortified drinks. An examination of the most appropriate solvent for the measurement of the phenolic and other antioxidants present will be made, along with the electrode conditions needed to make a reliable quantification. Comparisons will be made with standard Food Science antioxidant assays, and a wide range of beverages of different strengths will be surveyed.



1. P.A. Kilmartin and C.F. Hsu, "Characterisation of polyphenols in green, oolong, and black teas, and in coffee, using cyclic voltammetry", *Food Chemistry* **82** (2003): 501-512.
2. O. Makhotkina and P.A. Kilmartin, "Uncovering the influence of antioxidants on polyphenol oxidation in wines using an electrochemical method: cyclic voltammetry", *Journal of Electroanalytical Chemistry* **633** (2009) 165-174.
3. O. Makhotkina and P.A. Kilmartin, "The phenolic composition of Sauvignon blanc juice profiled by cyclic voltammetry", *Electrochimica Acta* **83** (2012) 188-195.
4. P.A Kilmartin, "Electrochemistry applied to the analysis of wine: A mini-review", *Electrochemistry Communications* **67** (2016) 39-42.

Localised interaction of PEDOT electrodes with antioxidants using Scanning Electrochemical Microscopy (SECM)

Prof. Paul Kilmartin
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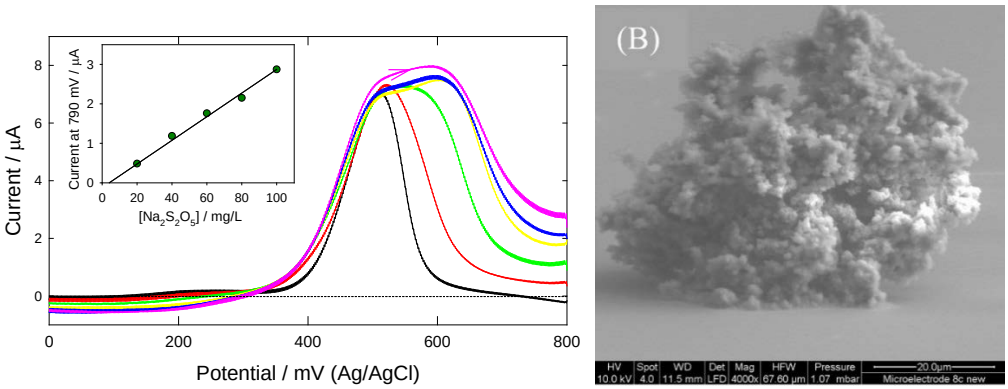
Conducting polymers are of considerable interest as plastics that conduct electricity. Their discovery by researchers including the New Zealander Alan MacDiarmid led to the award of the Nobel Prize in Chemistry in 2000. At the University of Auckland we have demonstrated that conducting polymers such as polyaniline are very efficient at scavenging free radicals, and in this sense act as solid antioxidant materials [1]. Further conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) have been found to be highly suitable for separating out the analytical signal due to different types of antioxidants present in beverages [2-4]. In this project the technique of scanning electrochemical microscopy (SECM) will be applied to different types of PEDOT electrodes prepared on gold substrates, and the interaction between PEDOT and beverage antioxidants will be examined in situ. If available, in situ electrochemical AFM will be applied as a further means to profile the electrode surface properties.



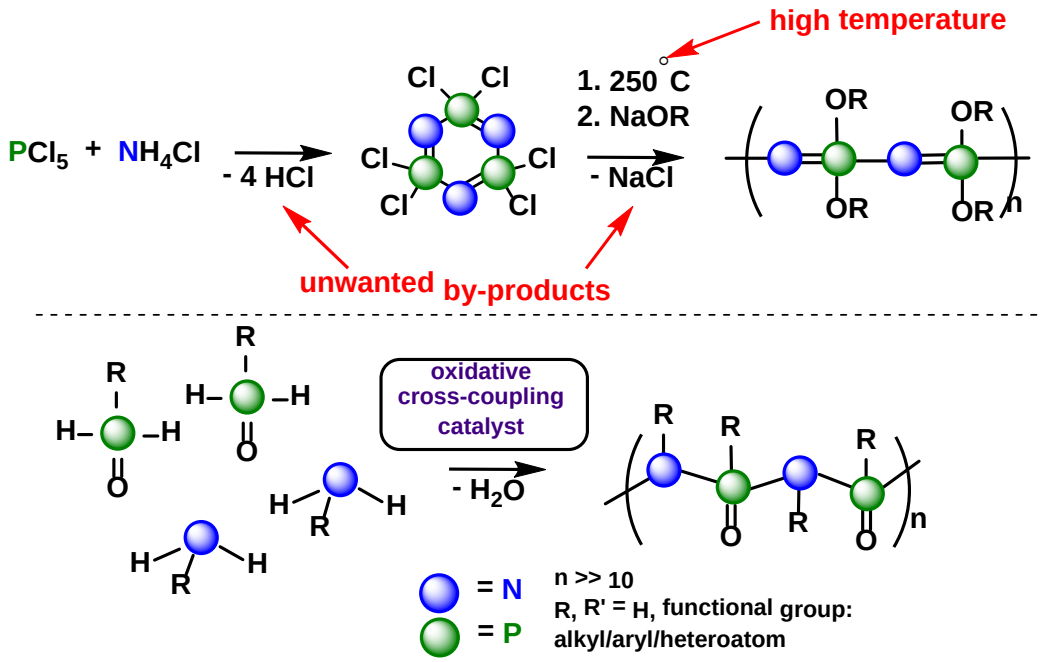
Current resposne of sulfite at PEDOT electrodes, and “fractal” growth of PEDOT on microelectrodes

1. A.V. Nand, S. Ray, A J. Easteal, G.I.N. Waterhouse, M. Gizdavic-Nikolaidis, R.P. Cooney, J. Travas-Sejdic and P.A. Kilmartin, “Factors affecting the radical scavenging activity of polyaniline”, *Synthetic Metals* **161** (2011) 1232-1237.
2. A. Türke, W.-J. Fischer, N. Beaumont, and P.A. Kilmartin, “Electrochemistry of sulfur dioxide, polyphenols and ascorbic acid at poly(3,4-ethylenedioxythiophene) modified electrodes”, *Electrochimica Acta* **60** (2012) 184-192.
3. H. Karaosmanoglu, W. Suthanthangjai, J. Travas-Sejdic and P.A. Kilmartin, “Electrochemical analysis of beverage phenolics using an electrode modified with poly(3,4-ethylenedioxythiophene)”, *Electrochimica Acta* **201** (2016) 366-373.
4. P.A Kilmartin, “Electrochemistry applied to the analysis of wine: A mini-review”, *Electrochemistry Communications* **67** (2016) 39-42.

Using catalysis to create new bioerodible materials useful in the construction of synthetic bone

Dr. Erin Leitao erin.leitao@auckland.ac.nz

Recent research demonstrates that polyphosphazenes are attractive bioerodible polymers postulated to be useful in the construction of synthetic bone. Polyphosphazenes are made from the ring opening polymerization of hexachlorocyclotriphosphazene $(Cl_2P{=}N)_3$ at high temperatures followed by functionalization by replacing the Cl atoms (see top scheme below; *e.g.* with RO, NRH, etc.). This synthesis suffers from the use of high temperatures, toxic reagents and large amounts of unwanted by-products. Copper-catalyzed oxidative cross-coupling (see bottom scheme below) has recently been shown to be an effective way to make P-N bonds from H-phosphonates $((RO)_2P(O)H)$ and amines $(R'NH_2)$. Expansion of this method in an attempt to make phosphoramidate polymers will be explored. The project will involve inorganic synthesis using various Cu(I) and Cu(II) catalysts with analysis and characterization using NMR spectroscopy and GC-MS. The project may also include the synthesis of a new active homogeneous catalyst useful for this process.



Understanding the mechanism of copper-catalysed cross-coupling with main-group substrates

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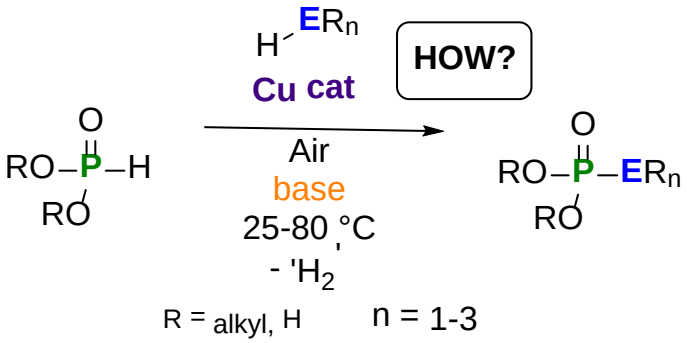
Compounds containing P-E bonds (E = N, S, O, P) expand a wide range of applications such as flame retardants, pesticides, coenzymes, as well as several bioactive molecules. Since the recent seminal reports of copper-catalyzed oxidative cross-coupling to furnish hypophosphates (P-P), pyrophosphates (P-O-P) and phosphoramidates (P-N) from H-phosphonates ($(RO)_2P(O)H$), there has been some expansion in the reaction scope using this methodology (including P-S bond formation), however, the mechanism(s) of the catalysis remain elusive. The seemingly simple and readily available catalysts (CuX_2 or CuX, *e.g.* X= halide, OAc, OMe) and substrates used in the majority of the transformations make this reaction attractive to study mechanistically (see Figure). Not to mention the elimination of byproducts such as H_2O (observed in some cases) and high selectivity in the P-N bond forming reaction (very little P-P, P-O-P products observed under the reaction conditions). Preliminary data suggests a homogeneous catalyst is in operation and forms more readily from the Cu(II) salts. Techniques such as: stoichiometric reactions, control reactions (*e.g.* absence of Cu catalyst, absence of a reagent, changing the order of addition), solvent and temperature studies, attempted synthesis of postulated intermediates and use of model complexes/analogues, will reveal pertinent details concerning the rate-determining step, potential transition states, and intermediates. This project will involve specially designed experiments to gain insight into the mechanism, along with analysis and characterization using NMR spectroscopy and GC-MS.



Catalytic routes to robust polysilanes

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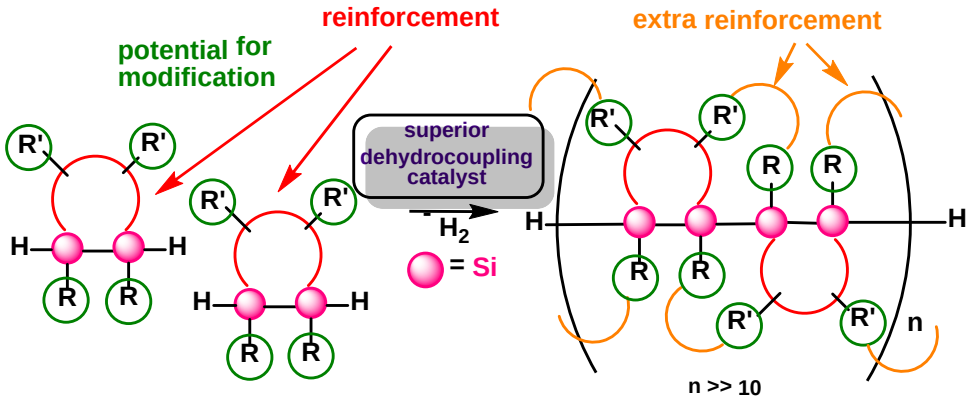
Polymers with a carbon backbone are ubiquitous. It is hard to go a day without coming in contact with one (polyethylene: *e.g. plastic bags, bottles, toys*; polypropylene: *e.g. dollar bills; thermal clothing*; polyisobutylene: *e.g. chewing gum, tires*). Polysilanes, polymers containing a Si-Si backbone, are in their relative infancy in terms of commercialization, but are highly sought after, as strong electronic σ-conjugation is achieved upon linear Si-Si chain formation giving rise to properties with a wide-range of potential applications (*e.g. photoconductors/initiators, explosive detecting materials, molecular recognition and information storage, semi-conductors suitable for modern energy generation*). Despite the first synthesis of polysilanes reported by Kipping nearly 100 years ago, and the growing interest in the utility of these materials, access to a mild and controlled synthetic method amenable to the large scale production of defect free (well-defined), strong (high molecular weight), high silicon content (extensive σ-conjugation) and tunable polysilane is non-existent. Of the current methods available to synthesize polysilanes, catalysis is the most promising. Catalytic dehydrocoupling is attractive because dihydrogen (H_2) is the only by-product and there is literature precedence for the formation of long chains of Si-Si atoms with primary silane substrates. To make robust polysilanes (see Figure), secondary silane substrates will need to be employed which is a significant challenge as strained Si-Si bonds are subject to disproportionation via Si-Si bond cleavage (much weaker than C-C bonds) producing low molecular weight oligomers. Furthermore, bulky substituents on the monomers can cause steric congestion at the metal-centre of catalyst as the chain grows limiting the chain length. A series of new catalysts will be assessed for this transformation using selected secondary silane substrates and the drawbacks illuminated during detailed investigations of the catalysis. The project will involve inorganic synthesis and analysis using NMR spectroscopy and mass spectrometery.



Development of novel inhibitors for *Mycobacterium tuberculosis* isocitrate lyase

Dr Ivanhoe Leung and A/Prof. Jonathan Sperry, School of Chemical Sciences

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Tuberculosis (TB) is an infectious disease that is caused by *Mycobacterium tuberculosis*. The World Health Organisation (WHO) End TB Strategy aims to reduce the mortality rate by 90% and the incidence rate by 80% by 2030. As *M. tuberculosis* can only spread from people who have developed active pulmonary TB, treatment of latent TB infection for people from high risk groups is a viable strategy to control the spread of the disease. Current medication regimens to treat latent TB infection require high patient compliance. In addition, these drugs have high toxicity. The development of more effective and less toxic drugs to treat latent TB infection are therefore required if we are going to meet the goals set out by the WHO.

Isocitrate lyase (ICL) is a metabolic enzyme of *Mycobacterium tuberculosis* that is important for the survival of the bacteria in the latent state. We are interested in the development of novel ICL inhibitors. This summer scholarship will form an integral part of this project, which will include the design and synthesis of ICL inhibitors, and *in vitro* characterisation of their inhibition potency against different isoforms of *Mycobacterium tuberculosis* ICL using biophysical techniques.

There is no formal prerequisites, although a keen interest in organic and medicinal chemistry and an enthusiasm in enzymology will be helpful. Training and supervision will be given throughout the summer period by both Dr Leung and A/Prof. Sperry. Please contact us by email if you require any more information.

References:

Bhusal, R.P.; Bashiri, G.; Kwai, B.X.C.; Sperry, J.; Leung, I.K.H. Targeting isocitrate lyase for the treatment of latent tuberculosis. *Drug Discov Today* **2017**, DOI: 10.1016/j.drudis.2017.04.012

Recombinant protein expression and purification

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Our research group is interested in the applications of biophysical techniques to study proteins and enzymes that are important for (1) human health and disease, and (2) New Zealand's agricultural industry.

A key step for any biophysical studies of proteins and enzymes involves the production and purification of recombinant proteins. In this project, you will be responsible for molecular cloning, conduct protein expression trials, optimise protein purification procedure and use biophysical tools including mass spectrometry and nuclear magnetic resonance spectroscopy to characterise the recombinant protein that you made.

There is no formal prerequisites to this summer scholarship, although an understanding of basic molecular biology and an enthusiasm in enzymology will be helpful. The work will be highly relevant to CHEM 350 and CHEM 390 in Stage 3. Training and supervision in molecular biology and enzymology will be given throughout the summer period. Please contact me by email if you require any more information.

Example of recent work from my group (including contribution from summer student):

Huang, R.; Ayine-Tora, D. M.; Muhammad Rosdi, M. N.; Li, Y.; Reynisson, J.; Leung, I. K. H. Virtual screening and biophysical studies lead to HSP90 inhibitors. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 277–281.

Research group website: http://leungresearchgroup.wordpress.fos.auckland.ac.nz/

Mechanistic and mutagenesis studies of grape (*Vitis vinifera*) polyphenol oxidase

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Polyphenol oxidases (PPOs) are type 3 di-copper enzymes that are widely found in both prokaryotes and eukaryotes. There are two main types of PPOs, including tyrosinase and catechol oxidase. Tyrosinase catalyses the oxidation of both monophenols and *ortho*-diphenols, whilst catechol oxidase only catalyses the oxidation of *ortho*-diphenols.

A number of structural and mechanistic studies were conducted in the last decade in order to understand the substrate selectivity of tyrosinase and catechol oxidase. Two proposals have emerged: One suggests the presence of a bulky 'blocker' residue above CuA may restrict PPO's monophenolase activity, whilst the other suggests that the amino acid residues that govern the entry of the substrate(s) to the active site are more important for selectivity. To date, the differences in substrate selectivity between these two closely related enzymes are still not fully understood.

By using grape (*Vitis vinifera*) PPO as a model system, we hope to understand the structural and mechanistic basis of PPO substrate selectivity. This summer scholarship will form an integral part of this project, which will include the design and production of mutant PPO, and *in vitro* kinetic characterisation of different substrates using biophysical techniques.

There is no formal prerequisites to this summer scholarship, although an understanding of basic molecular biology and an enthusiasm in enzymology will be helpful. The work will be highly relevant to CHEM 350 and CHEM 390 in Stage 3. Training and supervision in molecular biology and enzymology will be given throughout the summer period. Please contact me by email if you require any more information.

References:

1. M. Goldfeder, M. Kanteev, S. Isaschar-Ovdat, N. Adir, A. Fishman, Determination of tyrosinase substrate-binding modes reveals mechanistic differences between type-3 copper proteins, *Nat. Commun.* **2014**, *5*, 4505.

2. Bijelic, M. Pretzler, C. Molitor, F. Zekiri, A. Rompel, The structure of a plant tyrosinase from walnut leaves reveals the importance of "substrate-guiding residues" for enzymatic specificity, *Angew. Chem. Int. Ed.* **2015**, *54*, 14677–14680.

3. E. Solem, F. Tuczek, H. Decker, Tyrosinase versus catechol oxidase: one asparagine makes the difference, *Angew. Chem. Int. Ed.* **2016**, *55*, 2884–2888.

Research group website: http://leungresearchgroup.wordpress.fos.auckland.ac.nz/

Behaviour of fingermarks on ice

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We have reported that fingermarks can be deposited and recovered from ice and other difficult substrates, by staining with a dye that is soluble in fluorous solvents[1]. The fluorous solvents are ethers or alkanes in which all or a majority of the hydrogens are replaced by fluorine. They have significantly differently properties to the hydrogen-containing analogues, and are typically poor solvents for the components in sebaceous fingermarks. They also have low surface tensions, so do not cause physical alterations in sebaceous fingermark deposits.
This project will take advantage of these solvent properties in two ways. First, it allows us to stain fingermarks on substrates that are not suitable for other types of fingermark enhancement. Examples of these substrates might include salt-encrusted window or cold surfaces. The second part of the project will investigate whether it is possible to stain a fingermark and then monitor changes in the fingermark with time. These changes might include evaporation of components or diffusion across on into substrates.

1. Qi, L.; Miskelly, GM, Staining using the lipid dye LD540 in fluorous media: application to sebaceous fingermarks, Analytical ethods, 2015, 7, 1265-1268.

Hyperspectral imaging in chemical analysis

Associate Prof. Gordon Miskelly
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We have constructed a hyperspectral line imager suitable for imaging objects in the 1 mm – 10 cm size range. This project will apply this hyperspectral imager to systems in which spectral changes occur along one dimension.
Most students have used spectrophotometers in the laboratory, where solutions are placed in cuvettes (typically with a 1 cm pathlength) and their absorbance at one position in the cuvette at a specific wavelength is measured. Hyperspectral imaging measures the absorbance at multiple positions and many wavelengths simultaneously. For example, satellite-based hyperspectral imagers can map reflectance at many wavelengths around the world, and from that scientists can determine such features as mineral outcrops or vegetation types. Indeed, this type of imaging was used to support the first report of flowing liquid water on Mars.[1]
We perform hyperspectral imaging on a "laboratory scale", which ranges from the sub-mm ridges of a fingermark to the size of a footprint. We are determining the advantages of this imaging compared to standard colour photography, especially for forensic science applications. One possible application of these measurements is to monitor changes across a sample due to chemical reactions, diffusion or other physical changes. This project will investigate a selection of such systems depending on the interest of the student involved.
This project will require calculations using the Matlab programming environment.

1. Ojha, O. et al., Spectral evidence for hydrated salts in recurring slope lineae on Mars, Nature Geoscience, 2015, 8, 829-832.

The stability of microencapsulated cranberry powder

A/Prof Siew Young Quek sy.quek@auckland.ac.nz

This project will evaluate the stability of microencapsulated cranberry powder during storage, to verify if the method used is a satisfactory technique for the protection of the functional compounds in cranberry. The retention of anthocyanin, total phenolics and antioxidant activities will be evaluated after microencapsulation and during storage trials at different temperatures and relative humidity.

Applicant should have background in Food Science or Chemical Sciences, with chemical analysis skills and experience working in the lab environment. The project will start in November and estimated to last for about 3 months.

Correlation between predicted and measured hydrogen bonding energies in model systems

Jóhannes Reynisson

School of Chemical Sciences, University of Auckland, New Zealand

Hydrogen bonding is crucial biological systems, e.g., facilitating recognition between a substrate and an enzyme[1] as well as being the foundation of the genetic code.[2] It is therefore important that reliable theoretical methods are available to predict the hydrogen bonding energies such as the nucleotides in DNA.[3]

In this project a range of ab initio and density functional methods will be benchmarked against experimentally derived hydrogen bonding energies for model systems.[4-8] This will give us insight in the reliability of the quantum mechanical methods available for further application in biological systems.

[1] A. R. Fersht, *Structure and Mechnism in Protein Science*, W.H. Freeman and Company, New York, **1999**.
[2] J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737–738.
[3] S. Steenken, J. Reynisson, *Phys. Chem. Chem. Phys.* **2010**, *12*, 9088-9093.
[4] R. K. Thomas, *Proc. Roy. Soc. A* **1975**, *344*, 579-592.
[5] L. A. Curtiss, D. J. Frurip, M. Blander, *J. Chem. Phys.* **1979**, *71*, 2703-2711.
[6] A. C. Legon, D. J. Millen, H. M. North, *J. Chem. Phys.* **1987**, *86*, 2530-2535.
[7] A. C. Legon, *Chem.Phys.Lett.* **1978**, *55*, 157-159.
[8] A. C. Legon, D. J. Millen, H. M. North, *Chem.Phys.Lett.* **1987**, *135*, 303-306.

The redox potentials of pro-drugs activated with bio-oxidation/reduction as calculated with DFT

Jóhannes Reynisson

School of Chemical Sciences, University of Auckland, New Zealand

It is well known that many of the drugs currently in clinical use are activated via bio-oxidation or reduction.[1] E.g., mitomycin is an anticancer drug that has been in use for more than fifty years is activated by bio-reduction.[2] Many tumours are hypoxic and therefore designing drugs that are DNA damaging agents in their reduced form is an excellent strategy for making new potent anticancer drugs.[3, 4] In this project all drugs in clinical use, which are redox activated will be collected and their ionisation potentials (one-electron oxidation) and electron affinities (one-electron reduction) derived using the density functional theory (DFT). This will define a region in chemical property space that is acceptable and can be used for design purposes.

[1] P. A. Hume, M. A. Brimble, J. Reynisson, *Aust. J. Chem.* **2012**, *65*, 402-408.
[2] P. A. Hume, M. A. Brimble, J. Reynisson, *Comp. Theo. Chem.* **2013**, *1005*, 9-15.
[3] P. Yadav, A. J. Marshall, J. Reynisson, W. A. Denny, M. P. Haya, R. F. Anderson, *Chem. Commun.* **2014**, *50*, 13729-13731.
[4] R. F. Anderson, P. Yadav, D. Patel, J. Reynisson, S. R. Tipparaju, C. P. Guise, A. V. Patterson, W. A. Denny, A. Maroz, S. S. Shinde, M. P. Hay, *Organic & Biomolecular Chemistry* **2014**, *12*, 3386-3392.

The physicochemical parameters of veterinary drugs. A comparison study

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The concept of known drug space (KDS) is now well established for design of screening libraries and decision making in drug discovery projects.[1, 2] This volume in chemical space is characterised by the physicochemical parameters of the drug compounds as well as with certain unwanted chemical moieties.[3, 4] In this project veterinary drugs will be collected and analysed for their properties and functional groups. This will create a reference volume in chemical space to KDS and will give an idea of its positioning, i.e., is KDS unique or does it share the same/similar region as KDS?

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Lipopeptides as Antibacterial Coatings for Biofilm Eradication

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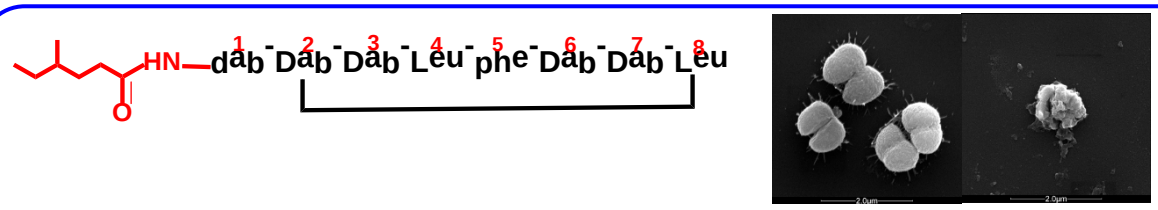
E-mail: v.sarojini@auckland.ac.nz

According to the World Health Organisation, the rapid emergence of multidrug resistant 'superbug' bacteria has created an urgent need to develop novel classes of antimicrobial agents. Unfortunately, over the last 30 years, no major types of antibiotics have been developed. Cationic antimicrobial peptides (CAPs) are promising therapeutics to address the challenge of bacterial resistance. The near success of MSI-78 (pexiganan acetate) and MX-226 or CPI-226 (Omiganan) in reaching the clinic, provide us with the enthusiasm to overcome the current roadblocks of CAPs (e.g. proteoclytic susceptibility) to achieve clinical implementation of AMPs.

To this end, we have developed several linear and cyclic lipopeptides with nonprotein amino acids which have shown low micromolar activity against bacterial pathogens and the ability to lyse bacterial membranes, both in solution and as antibacterial coatings.[1,2] This project will develop stereoisomers of our potent lipopeptides through chemical synthesis and investigate their potency, mechanism of action and their ability to self-assemble into antibacterial hydrogels.

Skills: The summer student working in this project will be trained in Synthetic Organic Chemistry, Solid Phase Peptide Synthesis, HPLC purification, Dynamic Light Scattering and Rheology measurements.



Lipopeptide sequence and cell morphology of *S. aureus* before (left) and after treatment

References

1. De Zoysa, G. H., & **Sarojini, V**. Feasibility Study Exploring the Potential of Novel Battacin Lipopeptides as Antimicrobial Coatings. *ACS Applied Materials & Interfaces*, (**2017**) *9*(2), 1373-1383. doi:10.1021/acsami.6b15859

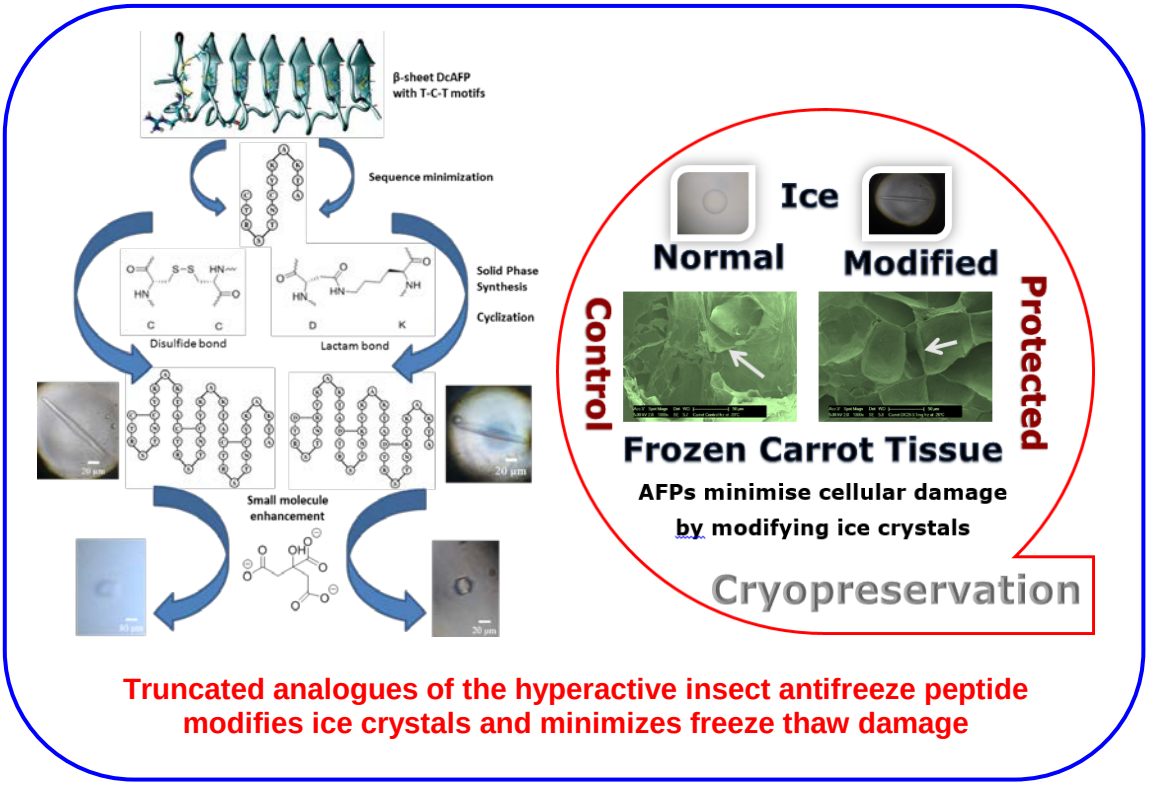
2. De Zoysa, G.H., Cameron, A., Hegde, V. V., Raghothama, S. and **Sarojini, V.** Antimicrobial Peptides with Potential for Biofilm Eradication: Synthesis and Structure Activity Relationship Studies of Battacin Peptides. *Journal of Medicinal Chemistry* (**2015**) 58, 625−639

Antifreeze Peptides for Preserving Texture in Frozen Foods

Dr Viji Sarojini, School of Chemical Sciences. E-mail: v.sarojini@auckland.ac.nz

Antifreeze proteins (AFPs) enable organisms like polar fish to survive the freezing temperatures of their natural habitat. AFPs have the ability to influence the size, morphology and aggregation of ice crystals which can be used in food technology, where the growth of ice crystals in frozen foods is of primary concern. AFPs expressed in yeast have been used in the ice-cream industry for creating a smooth texture and preserving ice crystal size distribution until consumption. Our recent work on hyperactive insect antifreeze peptides has been promising with shorter analogues showing ice crystal modification and ability to minimise freeze thaw damage in food.[1,2] Going deeper into the area, we aim to develop analogues of natural AFPs with enhanced antifreeze activity for fundamental mechanistic studies as well as potential applications in the frozen food industry. Ice crystal morphology studies and texture analysis of frozen fruits using the synthetic peptides will be done in collaboration with the Food Science group at UoA. This interdisciplinary project applies cutting edge peptide research to the needs of the frozen fruit industry which plays a major role in New Zealand's economy.

Skills: The summer student working in this project will be trained in Solid Phase Peptide Synthesis, HPLC purification and food science techniques relevant to the project.



Truncated analogues of the hyperactive insect antifreeze peptide modifies ice crystals and minimizes freeze thaw damage

References

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Cell Penetrating Peptide Nanoparticles for Drug Delivery

Dr Viji Sarojini, School of Chemical Sciences. E-mail: v.sarojini@auckland.ac.nz

Increase in the number of new therapeutics that fails to reach the clinic due to poor delivery has made novel drug delivery systems an important consideration in therapeutic development. Cell penetrating peptides (CPP) are promising tools for delivering biologically active molecules like oligonucleotides and proteins into cells.[1] The carrier-biomolecule (cargo) interactions are dictated by the sequence of the CPP. Mechanism of cellular drug internalization by CPPs is not well understood. This project aims to develop short synthetic peptides derived from the *trans*-activating regulatory protein (TAT) of the human immunodeficiency virus (HIV) which is the first known CPP ever. The TAT sequence will be synthesized by Solid Phase Peptide synthesis and conjugated to short oligonucleotide chains. It is expected that the peptide-oligonucleotide complex will form stable nanoparticles facilitating the entry of the drug into the cell through the plasma membrane. Morphological features of the CPP-oligonucleotide complex will be investigated by scanning electron microscopy (SEM) and light scattering measurements in collaboration with Prof Jadranka Travas-Sejdic. This project also involves collaboration with the Auckland Cancer Society Research Centre.

Skills: The summer student working in this project will be trained in Solid Phase Peptide Synthesis, HPLC purification and spectroscopic techniques such as NMR and Circular Dichroism and nanoparticle synthesis and analyses.

General scheme of peptide drug conjugate system

Reference

1. Dissanayake, S., Denny, W. A., Gamage, S., & **Sarojini, V**. Recent developments in anticancer drug delivery using cell penetrating and tumor targeting peptides. *Journal of Controlled Release*. (**2017**) 250, 62–76 doi:10.1016/j.jconrel.2017.02.006

Antimicrobial Peptides against Food Spoiling Psychrophiles

Dr Viji Sarojini and A/P Siew-Young Quek, School of Chemical Sciences. E-mail: v.sarojini@auckland.ac.nz

Psychrophilic bacteria (refrigerator bacteria) are cold-adapted organisms, found widely over the earth's surface due to the vast number of habitats in which they can grow. Psychrophilic bacteria have also been found to grow in refrigerators, which is of great concern to the food industry. In particular, meat products have been found to be affected and spoiled by psychrophilic growth.[1] An important psychrophile is the species *Clostridium estertheticum*, which has been found to cause blown pack meat spoilage in chilled vacuum-packed meat products. As New Zealand has a prominent meat industry, in particular of beef and lamb exports, targeting psychrophilic species such as *C. estertheticum* would be economically beneficial. This project will explore the potential of naturally produced antimicrobial peptides of the ice fish *Chionodraco hamatus* to inhibit the growth of *Clostridium estertheticum* in meat products. Promising peptide analogues will be used in combination with food packaging technologies in collaboration with A/P Quek, Director of the Food Science Programme.

Skills: The summer student working in this project will be trained in Solid Phase Peptide Synthesis, HPLC purification, anti-bacterial and anti-biofilm assays, microscopy techniques as well as spectroscopic techniques such as NMR and Circular Dichroism.

References

1. Danilo Ercolini, Federica Russo, Antonella Nasi,Pasquale Ferranti and Francesco Villani. Mesophilic and Psychrotrophic Bacteria from Meat and Their Spoilage Potential In Vitro and in Beef. *Appl Environ Microbiol.* (**2009**) 75(7): 1990–2001.

De novo Designed Models of Protein β-sheets

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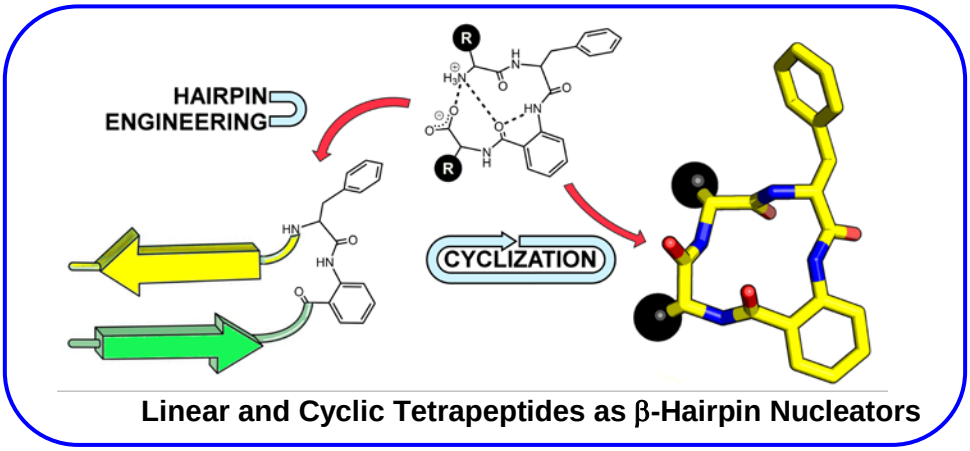
The remarkable biological functions exhibited by proteins depend on the ability of the flexible peptide chains to fold into well-ordered and compact structures that originate with distinct secondary structural elements like alpha-helices and beta-sheets discovered by Linus Pauling half a century ago. Thus, the *de novo* design of protein secondary structures is an important step towards understanding the biological functions of proteins in living cells. Amongst the protein secondary structural elements, beta-sheets (aggregates of beta hairpins) are particularly interesting, since they ensure not only protein function but also mis-function as in the case of amyloid plaque formation in Alzheimer's disease.[1-2] This project aims to understand the factors that modulate the formation and stability of beta-sheets which are not well understood through the design of novel β-hairpins using designed β-turn motifs.

Cyclic tetrapeptides (CTP) are attractive candidates in this regard.[3] The diagram below shows an example of a β-hairpin structure based on anthranilic acid containing CTPs recently developed in the group. Novel CTP templates will be designed and their ability to fold into the desired β-hairpin fold as well as their propensity to aggregate into higher order structures will be investigated using multi-dimensional NMR and circular dichroism (CD).

Skills: The summer student working in this project will be trained in Synthetic Organic Chemistry, Peptide Design, Solid Phase Peptide Synthesis, HPLC, NMR and CD.



Linear and Cyclic Tetrapeptides as β-Hairpin Nucleators

References

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New Enzymes for Water Treatment

Dr Viji Sarojini and Prof James Wright, School of Chemical Sciences (Centre for Green Chemical Science) E-mail:v.sarojini@auckland.ac.nz

In developing as well as developed nations, a growing number of contaminants are entering the aqueous environment from human activity. Organic herbicides/pesticides for controlling weeds, insects and fungi in agriculture comprise the largest group of xenobiotic compounds deliberately introduced into the environment. These compounds, and their metabolites end up in drinking water at concentrations exceeding the 0.1µg/L threshold of pesticide residues in drinking water. This translates into an immediate need for effective, low-cost, robust water treatment methods to remediate waters without further stressing the environment or endangering human health. This project aims to undertake the basic research to develop biodegradable peptide-based scavenger enzymes for water remediation applications.

Skills: The summer student working in this project will be trained in Molecular Modelling, Solid Phase Peptide Synthesis, HPLC purification and residue scavenging techniques relevant to the project.

Anti-Biofilm Peptide-Polymers for Water Disinfection

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Billions of people lack access to safe drinking water and millions die annually from diseases transmitted through the consumption of unsafe water. Waterborne infectious agents causing such diseases include bacteria, fungi, protozoa and viruses. Viruses are of particular concern and account for half of the emerging pathogens in recent times. The main water disinfectant used worldwide, free chlorine, is ineffective in controlling certain waterborne pathogens, particularly *Mycobacterium avium*, ubiquitous in biofilms found in water distribution systems. *Campylobacter* is a disease causing Gram negative bacterium detected last year in contaminated waters in Havelock North which led to a severe outbreak of gastro illness in the town. Growing of biofilms within ageing water distribution systems is a significant challenge facing infrastructure providers across the world. Using our previous experience in developing antimicrobial peptides for biofilm control, this project aims to develop antimicrobial peptides with potency and selectivity towards *Mycobacterium avium* and *Campylobacter* biofilms found in water distribution systems.

Skills: The summer student working in this project will be trained in Solid Phase Peptide Synthesis, HPLC purification and microbiology techniques relevant to the project.

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http://www.radionz.co.nz/news/national/312100/gastro-bug-hit-5000-in-havelock-north

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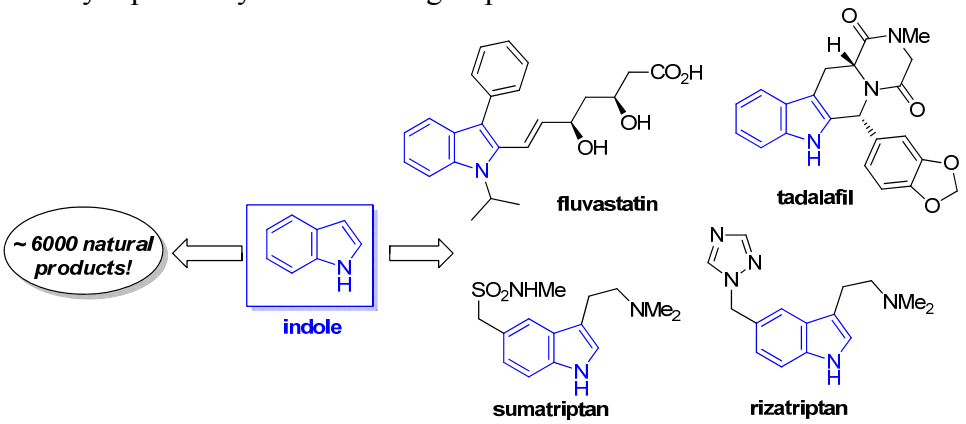
Associate Professor Jonathan Sperry

Room 727A. Ph. Extn: 88269, E-mail:j.sperry@auckland.ac.nz

1. Novel Synthetic Methods for Indole Construction

The indole ring system represents one of the most abundant and important heterocycles in nature, with over 6000 natural products possessing this ring system. Additionally, drugs containing the indole heterocycle below accounted for nearly US$8 billion in sales annually. In keeping with their importance, the development of new routes towards indoles is a central theme and ongoing challenge in contemporary organic synthesis.[1] This project aims to develop a novel indole synthesis using some intriguing transition metal chemistry recently reported by our research group.[2]



1. Inman, M.; Moody, C. J. *Chem. Sci*. **2013**, *4*, 29.
2. Wang, C.; Sperry, J. *Chem. Commun*. **2013**, *49*, 4349.

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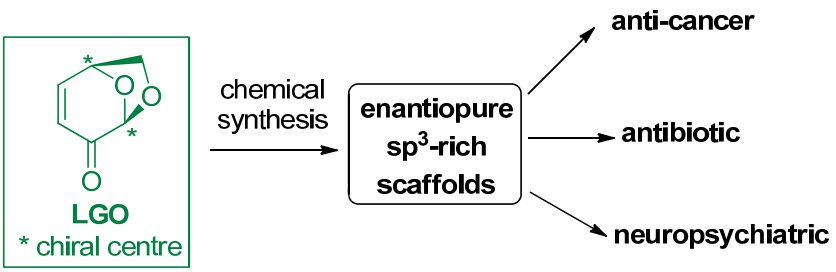
2. Sustainable Medicinal Chemistry with Biomass-Derived Building Blocks

Recent advances in sp^2-couplings have resulted in the synthesis of 'flat' molecules becoming the mainstay of drug discovery programmes. As a result, the field is slowly moving away from the 'flatlands' and towards saturated, sp^3 rich compounds capable of exploring novel, three dimensional chemical space. Molecules containing a high fraction of sp^3-hybridised carbon atoms and numerous stereocentres have a lower rate of attrition during the drug discovery process, thus providing higher-quality lead compounds. When also considering that the global chemistry community must reduce its reliance on fossil fuels and employ molecules derived from biorenewable sources in the production of society enhancing chemicals, sustainable methodologies that provide stereodefined, "sp^3-rich" scaffolds will underpin future advances in small molecule drug design. The summer research student will investigate the cellulose-derived molecule levoglucosenone (LGO) as a platform for the synthesis of several biorenewable sp^3-rich scaffolds. All of the new compounds synthesised in this project will be subjected to a detailed biological evaluation for anti-cancer, anti-microbial and neuropharmacological properties through international collaborators.



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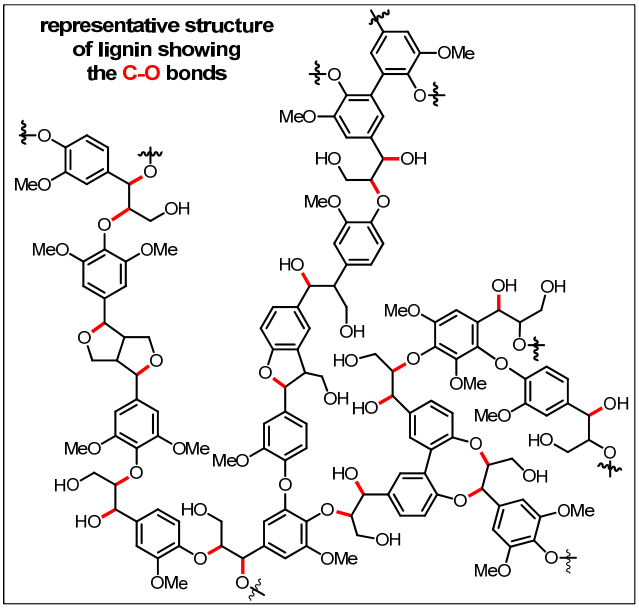
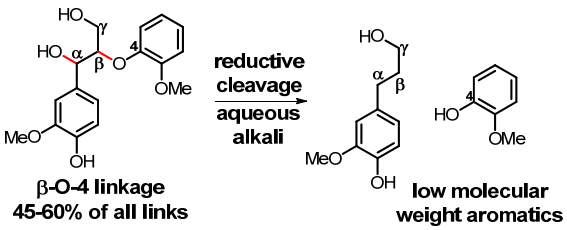
3. New Chemical Technologies for the Depolymerisation of Lignin

Fossil fuels are the carbon feedstock that modern society relies upon for the production of fuels and fine chemicals. Besides the environmental impact from their extraction and processing, fossil fuels are a finite resource for which there are currently no sustainable alternatives. Biomass is the only renewable carbon feedstock that could potentially replace fossil fuels and the efficient conversion of biomass into fuels and fine chemicals on a global scale is one of the great scientific challenges of the 21st century. Lignocellulosic biomass (dry plant matter) is the most abundant renewable carbon resource on earth, with an annual growth in the region of 200 billion tonnes. The separation of lignocellulosic biomass (wood pulping) produces the cellulosic fraction and the lignin fraction. The cellulosic fraction is amenable to chemical and enzymatic degradation techniques and its conversion into useful monomers is relatively well advanced. On the other hand, the large-scale potential of lignin is mostly limited to use as a low value fuel in pulp mills. As an aromatic biopolymer, lignin is an ideal candidate to meet future demand for aromatic commodity chemicals (phenols, benzene, xylenes, BTX etc) and other marketable aromatic products. This project will investigate novel reductive methods for the depolymerisation of lignin, specifically targeting the β-O-4 linkage that comprises up to 60% of the lignin linkages.





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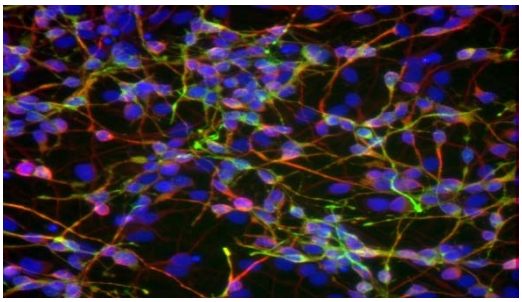
4. Synthesis of Small Molecules that Influence PSA-NCAM: Potential Therapeutics for the Prevention of Glioblastoma Metastasis

Neural cell adhesion molecules (NCAM) are involved in neural plasticity, cell migration, cell-cell adhesion etc. When attached to a polysialic acid (PSA) motif, the resulting PSA-NCAM complex promotes cell migration and is thought to play a pivotal role in the metastasis of glioblastomas (brain tumours).[1] In collaboration with the Centre for Brain Research at the University of Auckland, we have developed a library of small molecules that lower PSA-NCAM levels, but by an (as yet) unknown mechanism. This project will involve the chemical synthesis of further compounds that will help unravel the exact mechanism of action, an important step towards the goal of developing therapeutics that target the PSA-NCAM complex.



(neural stem cell derived neurons; PSA-NCAM in red)

1. Amoureux MC, Coulibaly B, Chinot O, Loundou A, Metellus P, Rougon G, Figarella-Branger D (2010) Polysialic acid neural cell adhesion molecule (PSA-NCAM) is an adverse prognosis factor in glioblastoma, and regulates olig2 expression in glioma cell lines. BMC Cancer 10:91

Atomic force microscopy on polymers

Professor Jadranka Travas-Sejdic
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In this project, the student will study polymeric structures using atomic force microscopy (AFM). AFM is a technique that used to look at nanometer scale structures. Different types of polymers, such as block copolymers and graft copolymers, can form different structures depending on how the samples are prepared. For example, spincoating a diblock copolymer can lead to micelles with either of the two polymer blocks inside the core, depending on which solvent is used. This will give us more information on the behaviour and properties of our polymers.

The type of polymers that will be studied in this project are graft copolymers with an electrically conducting backbone. By preparing these polymers with different types of side chains, conducting materials with special properties can be made. Our goal is to make a flexible, stretchable, self-healing and adhesive conducting polymeric material that can be easily processed. For the optimization of these materials, it is essential to know how they behave in different environments. This project will help us understand more about these polymers and the type of structures they can form, and how this relates to the electrical and mechanical properties of the material.

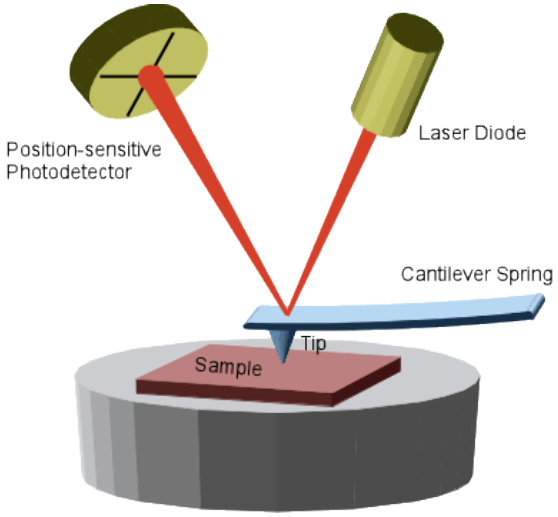

Figure 1. Working mechanism of an atomic force microscope. (source: https://physik.uni-greifswald.de/en/biophysics-and-soft-matter-prof-christiane-helm/methods/afm-atomic-force-microscope/)

Skills required: basic knowledge on polymers, steady hands are needed to operate the AFM

Electrospinning Conducting Rubbers

Professor Jadranka Travas-Sejdic
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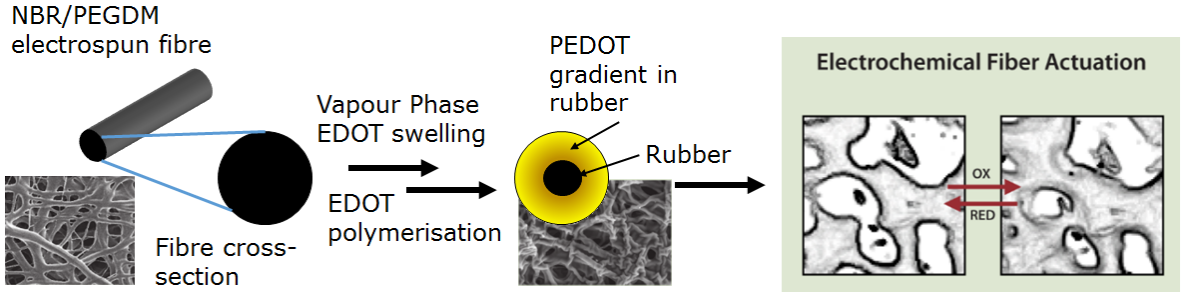
Electrospinning is a versatile technique used to produce continuous nanofibers. It is currently used commercially to produce air filter membranes and tissue engineering scaffolds. This projects aims to electrospin chemically modified rubbers and then embed the resulting fibres with conducting polymer, PEDOT. The challenge will lie in electrospinning a rubber, as rubbers have T_g's below room temperature. This causes the fibres to fuse and flatten, forming a film.
The chosen candidate must overcome this limitation through careful use of support polymers and solution conditions. The modified rubbers will be characterised through FTIR and tensile testing, and the resulting fibres will need to be characterised with SEM and their electrochemical properties analysed through techniques such as cyclic voltammetry and a four-point probe conductivity measurements.

This project will be based off the previously published work by Thomas Kerr-Phillips et al.[1]



1. T. E. Kerr-Phillips, V. Woehling, R. Agniel, G. T. Nguyen, F. Vidal, P. Kilmartin, C. Plesse and J. Travas-Sejdic, *Journal of Materials Chemistry B*, 2015, **3**, 4249-4258.

Surfaces for Dynamic Microfluidics

Supervisor: Dr Geoff Willmott (g.willmott@auckland.ac.nz)

The impact of nanotechnologies and microfluidic devices on society is becoming more and more significant. In these fields, materials behave differently from bulk materials, and devices operate in different ways to similar large-scale devices. One important reason for this is the high ratio of surface area to volume at small length scales. Often, surfaces form an interface between a solid and a moving fluid.

Experimental projects are available in which solid surfaces are chemically altered in order to control their interactions with adjacent, moving fluids at small length scales. High-speed photography is an important tool for characterizing the flows, for example in capillary uptake, or by following the paths of tracer particles. Examples of surfaces that may be functionalized include (i) spherical beads, which may be asymmetrically coated to create 'Janus' microparticles that self-assemble into interesting structures, (ii) capillary tubes, which are relevant to development of microfluidic devices, and (iii) substrates used on a quartz crystal microbalance. Suitable for chemistry students with good quantitative skills.

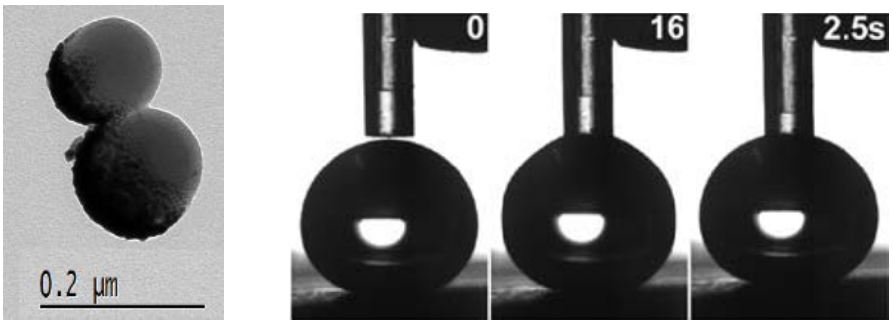


Figure: Left, Janus beads prepared by thermal evaporation of gold onto glass. Right, high speed sequence showing a water drop interacting with a PTFE capillary (time labelled in ms for the first two frames).

Metallabenzenes as building blocks for new materials

Supervisor: L. J. Wright (http://www.che.auckland.ac.nz/staffsites/WrightJ/index.html)

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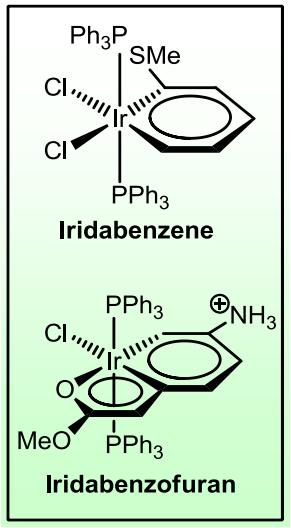
Metallabenzenes are compounds in which one of the CH groups of benzene has been formally replaced by a transition metal with its ancillary ligands. The first example of a metallabenzene, an osmabenzene, was synthesised at the University Auckland. We are interested in exploring the syntheses, reactivity and bonding of this intriguing new class of compounds and have an active research programme in this area. Summer Scholarship projects will involve the investigation of routes to functionalised metallabenzenes that will serve as precursors for the fabrication of new materials. Particular targets are conducting polymers that contain the metallabenzene unit as part of the polymer backbone and two-dimensional sheets that are comprised of fused-ring metallabenzenes that can be viewed as nascent metallagraphenes. The projects will enable experience to be gained in a broad range of areas including synthesis, spectroscopy (especially NMR, IR, ESMS), and X-ray crystallography.



Water purification by catalytic oxidation of pollutants

Supervisor: L. J. Wright (http://www.che.auckland.ac.nz/staffsites/WrightJ/index.html)

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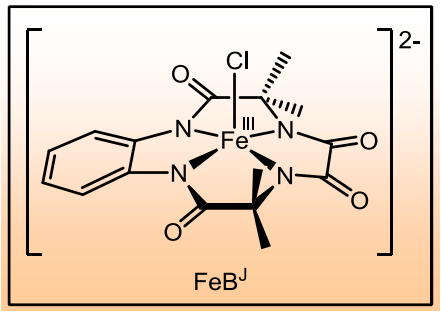
Oxidation chemistry plays a central role in many key processes including fine chemical and commodity chemical manufacture, bleaching, waste remediation and disinfection. The use of the environmentally benign oxidant hydrogen peroxide in these processes is very attractive, but it reacts very slowly with most organic compounds under ambient conditions. Appropriate oxidation catalysts are therefore needed. In a joint Green Chemistry programme with Carnegie Mellon University in the USA, we are investigating the applications of a series of new iron complexes (TAMLs) that efficiently catalyse hydrogen peroxide oxidations. The Summer Scholarship project involves studies of these iron compounds as catalytic oxidants in a new solid state technology we have developed for the oxidative destruction of dilute organic pollutants in water. Oxidative removal occurs without contamination of the water with hydrogen peroxide, catalyst or base. The project will enable experience to be gained in a broad range of areas including synthesis, spectroscopy and analysis (especially using NMR, IR, UV-vis, ESMS and HPLC).



CO-Releasing Molecules with Targeted Pharmacological Activity

Supervisors (joint): L. J. Wright and C. Hartinger

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It has recently been established that carbon monoxide (CO) plays a key role as a gaseous messenger in the human body. At very low concentrations CO has been shown to elicit protection and beneficial outcomes against inflammation, apoptosis (including cancer cells), cell proliferation, and oxygen reperfusion damage. Accordingly, there is rapidly growing interest in the potential therapeutic applications of CO. Since administration of CO gas through inhalation is not feasible because of its lack of selectivity and high general toxicity when overdosed, there is a strong research drive to develop water soluble transition metal (TM) compounds that can bind CO and release it inside the body in a controlled way. Current CO-releasing molecules (CORMs) of this type release CO either by hydrolytic or photolytic processes. There is a clear need for the development of CORMs that are selectively activated by certain tissue types. We are currently developing special ligands for metal carbonyl complexes that will show this tissue selectivity and only release CO in target tissues such as those found in solid tumours or in the heart after cardiac arrest. The project will involve the synthesis of selected examples of these special ligands, the formation of metal carbonyl complexes of these ligands and the study of CO release from these. The project will enable experience to be gained in a broad range of areas including synthesis, spectroscopy and analysis (especially using NMR, IR, UV-vis, ESMS and HPLC).