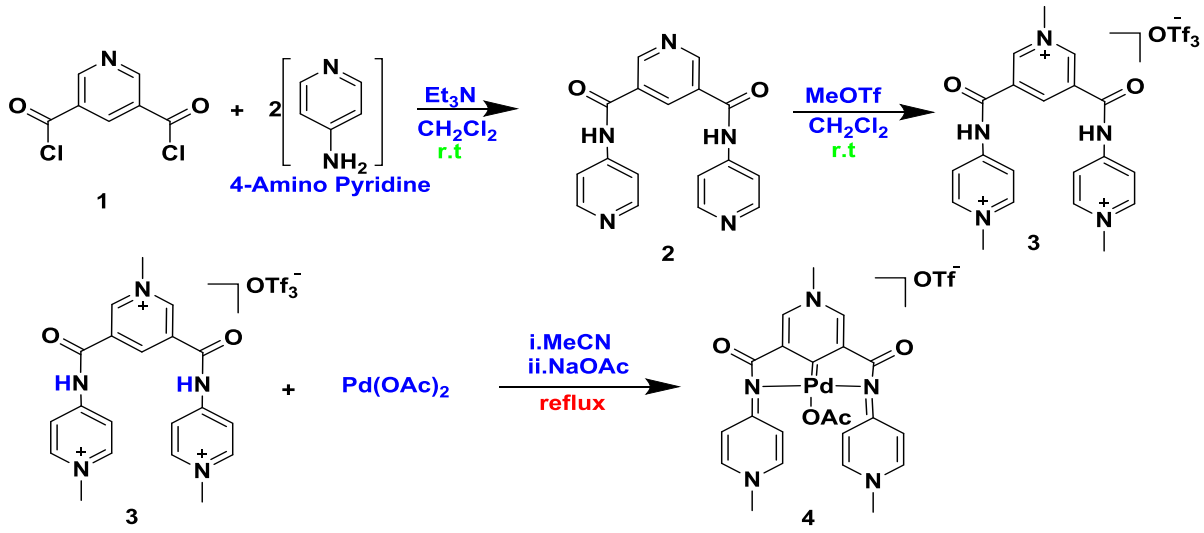
Poster 1

Synthesis of the First Tridentate Ligand that incorporates both Pyridinylidene Amide (PYA) and Remote *N*-Heterocyclic Carbene (*r*NHC) donors groups

Ayiya B. Bitrus
L. James Wright

Our focus is to develop a new series of strong electron donor ligands that are anticipated to give rise to electron rich metal complexes vital for applications in homogeneous catalysis. Ligands with pyridinylidene amide (PYA) and *N*-heterocyclic carbene (NHC) donor groups form an interesting subclass of strongly donating ligands. It has been shown that the flexibility and varying degrees of electron donor ability of these ligands can stabilize the transition metal catalysts in several catalytic organic and organometallic reactions.[1-4] However, ligands that feature both remote *N*-heterocyclic carbene (*r*NHC) and PYA donors have not been reported previously. In *r*NHCs, the nitrogen heteroatom is not located next to the carbene carbon within the carbocyclic ring, but instead is distant or remote from it. In a development of this concept, we have synthesised the target multi-dentate pro-ligand **3** through the condensation reaction of 3,5-pyridinedicarbonyl dichloride **1** with 4-Amino pyridine in the presence of a base to give **2** followed by reaction with methyl triflate to alkylate the pyridine nitrogen atoms and give **3**. Deprotonation of the amide nitrogen of **3** and thermal C-H activation with a palladium(II) precursor in the presence of sodium acetate under reflux in acetonitrile, cleanly affords the *r*NHC-PYA palladium(II) metal complex **4**. This compound has been unambiguously characterized by NMR and infra-red spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallographic studies.



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Poster 2

Comparing Some Physico-Chemical Properties of Caseinates Obtained from A2 Milks and Normal Milk

Weam S. Banjar

Yacine Hemar

Different genetic variants exist within different milk proteins, which might affect the functional properties of the milks. Beta-casein has 13 different genetic variants, and A1 and A2 are the most common variants among them. The difference between those two genes is one amino acid in β-casein chain at position 67. There has been a large number of ongoing debate about how A2 milk is beneficial for human health. However, there has been limited studies on the physico-chemical properties of these milks or on ingredients obtained from these milks. In this study, A1A2 milk, containing both A1 and A2 β-casein, and A2 milk containing only A2 β-casein variant, are considered. Sodium caseinates were obtained from A1A2 and A2 milks and investigated using liquid chromatography coupled with tandem mass spectrometry (**LC− MS/MS**), rheology and light and x-ray scattering methods. Sodium caseinates were dissolved in Double distilled water (ddH2O) at concentrations ranging from 0.01 to 10%. Particle size and rheological results showed clearly that the properties of the caseinate solutions are the same, which would strongly indicate that the overall functionality of caseinates is not affected by the β-casein genetic variant.

Poster 3

RSoXS – A Powerful New Tool for Probing Photonic Crystal Architectures

Andrew Chan
Isvar Cordova[1], Gregory Lumpkin[2], Dongxiao Sun-Waterhouse, Geoffrey Waterhouse
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[2]*Institute of Materials Engineering, Australian Nuclear Science and Technology Organization, Lucas Heights, New South Wales, Sydney, Australia*

The periodic structure of inverse opal photonic crystals creates photonic band gaps (PBGs), which can be exploited to enhance the performance of semiconductor photocatalysts for various photoreactions via a phenomenon known as the *slow photon effect*. Literature reports of the *slow photon effect* in metal-oxide inverse opal photocatalysts typically employ *ex-situ* characterisation methods, which creates ambiguity when attempting to establish firm structure-activity relationships.[1] Resonant Soft X-ray Scattering (RSoXS) is a recently developed synchrotron technique that combines small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) allowing for multimodal detection of electronic ordering phenomena emerging and buried at interfaces (i.e. sites of catalysis). Here, TiO_2 inverse opal thin films with PBGs at 400 nm (near the slow photon operating regime) were successfully fabricated by colloidal crystal templating onto Si_3N_4 substrates. The films comprised a face centred cubic (fcc) array of macropores in a nanocrystalline anatase TiO_2 matrix whose [111] growth direction is perpendicular to the underlying substrate. Preliminary RSoXS data in Figure 1 show scattering features comparable to the dimensions of the various features seen by scanning electron microscopy (SEM) for the TiO_2 inverse opal. Future work will utilize the recently developed *in-situ* RSoXS/TEM holder for *in-operando* photoelectrochemical hydrogen and oxygen gas evolution from alcohol-water mixtures under AM 1.5 G solar irradiation.

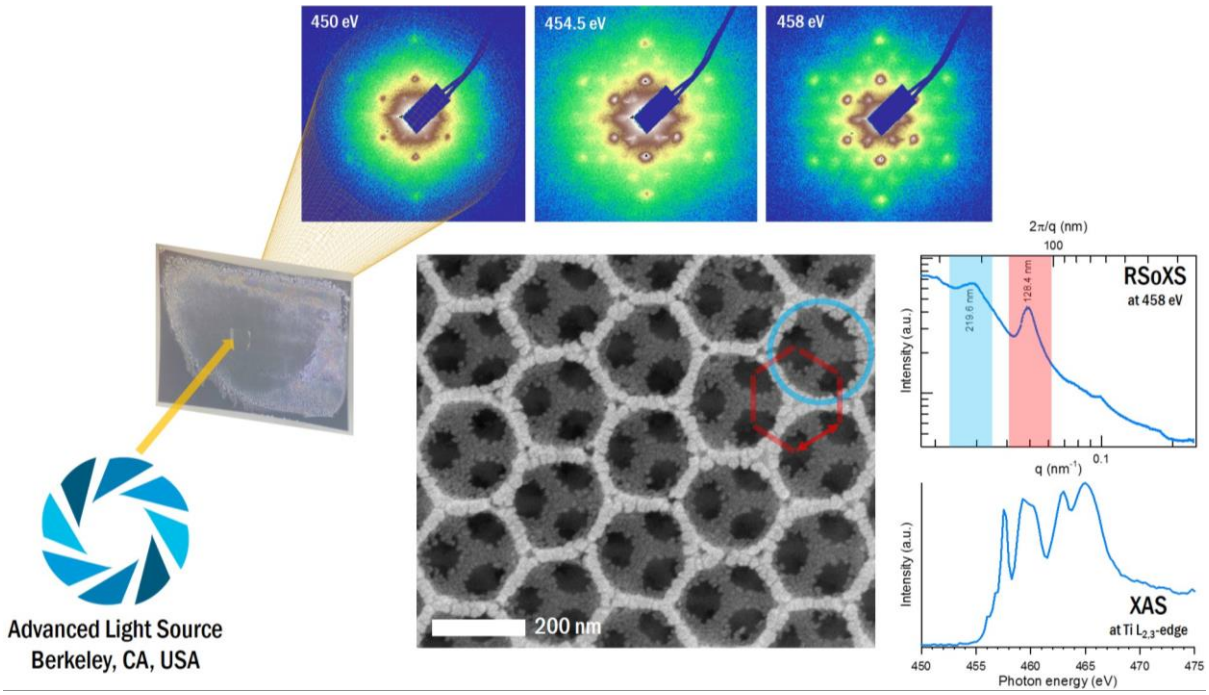

Figure 1. (Top) RSoXS images collected a various X-ray photon energies over the Ti $L_{2,3}$-edge. (Centre) SEM image of a TiO_2 inverse opal, showing a *fcc* array of macropores. Coloured shapes corresponding to scattering features seen in the reduced RSoXS pattern collected at 458 eV (right).

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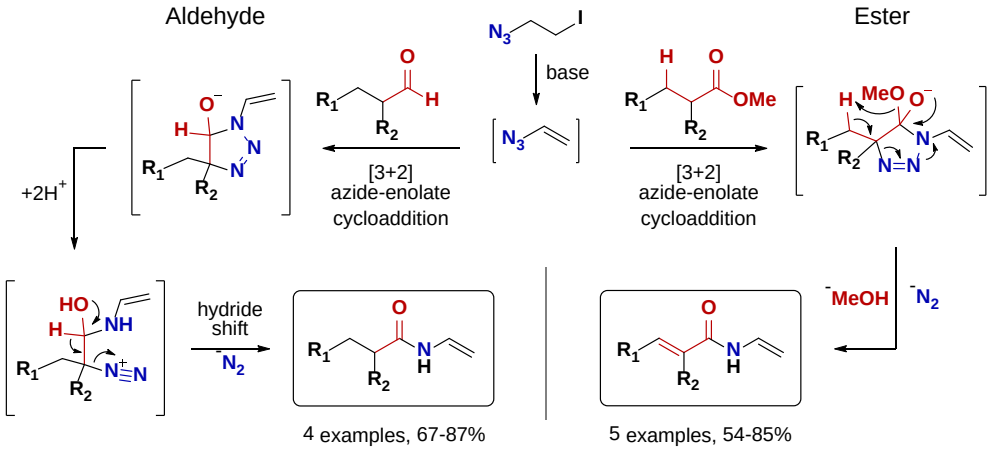
Poster 4

Direct *N*-vinyl amide synthesis via an unexpected [3+2] enolate-vinyl azide cycloaddition.

Hans Choi, Harry J. Shirley, Paul A. Hume, D. Prof. Margaret A. Brimble, Dr Daniel P. Furkert



En route to a series of α-quaternary carbonyl derivatives, treatment of α-substituted aldehydes or esters with azidoiodoethane and base was remarkably found to cleanly deliver *N*-vinyl acrylamides.[1] This unexpected reaction appears likely to proceed *via* initial [3+2] azide-enolate cycloaddition, to form a 1,2,3-triazoline intermediate,[2] which then undergoes a hydride shift (for aldehydes) or β-deprotonation (for esters) to generate the product *N*-vinyl amides. Control experiments suggest that this process occurs through *in situ* generation of vinyl azide which is also demonstrated computationally to be a highly reactive substrate for the cycloaddition.[3]

N-vinyl amides are valuable intermediates for synthesis and industrially important monomers for poly(vinylamide)s.[4] Exploration of *N*-vinyl amide chemistry and the applications of poly(vinylamide) materials is currently limited by the lack of general access to the requisite monomers.[5] We expect that the reaction reported here will accelerate investigation of this compound class. The mechanistic insights revealed in this study will also contribute to the growing area of direct amide synthesis.

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Poster 5

mRNA translation in Parkinson's disease

Danilo Correddu and Ivanhoe K. H. Leung

Parkinson disease (PD) is a chronic and neurodegenerative disorder characterised by loss of neurons that produce dopamine, a hormonal transmitter responsible for the coordination of body movements.[1] Although the causes of most PD are unknown, mutations in the leucine rich repeat kinase 2 (LRRK2) gene were found to be highly correlated to the familial forms of PD.[2] The most common mutation is a glycine to serine amino acid substitution at position 2019 of the kinase domain of LRRK2, which increases its activity and modifies protein translation. In vitro and in vivo studies have shown that the ribosomal protein S15 is a substrate of LRRK2, which upon phosphorylation causes translation dysfunction and subsequent neurodegeneration.[3,4]

Our aim is to understand how the phosphorylation of S15 is connected to malfunction in mRNA translation and alteration of protein homeostasis. We employ molecular biology methods and a range of biophysical techniques to investigate the biochemistry and structure of S15 in order to provide knowledge for the development of new pharmaceutical compounds.

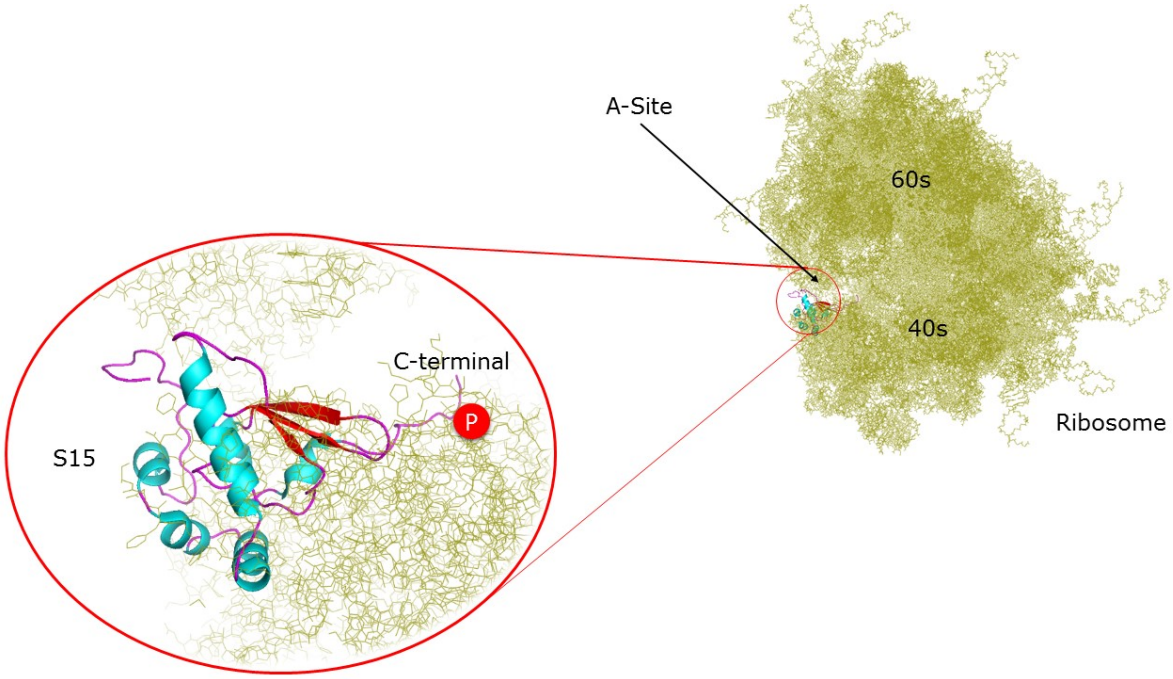

Figure 1. Ribosomal protein S15 in the ribosome. The phosphorylation of S15 occurs in the C-terminal tail which may interact with other ribosomal proteins, assembly and translational factors, mRNA and tRNA during translation.

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Poster 6

Synthesis and Evaluation of Menaquinone D (MenD) Inhibitors as Potential TB Therapeutics

Shaun Ferris

Distinguished Prof. Margaret Brimble, Dr. Dan Furkert

Menaquinone (MQ) is a lipid soluble electron carrier, central to normal function of the electron transport chain of *Mtb* and other gram-positive bacteria, in both latency and active growth. It presents a potentially useful therapeutic target as it is not produced in humans. Building on the essential role of MenD in *Mtb* survival and the established effectiveness of MenA inhibitors, a series of putative MenD inhibitors are being designed to explore the potential utility of MenD as a therapeutic target.[1]

Using a number of complementary approaches, several series of inhibitor candidates are in preparation. These approaches are informed respectively by; the results of commercial and in-house library screening, *in silico* modelling studies, and rational design informed by crystallographic data from key intermediates in the MenD-catalysed transformation of isochorismate. Progress in design and organic synthesis of inhibitor candidates will be presented, with a current summary of information gained through *in silico* compound docking, crystallography and kinetic assay data against MenD.

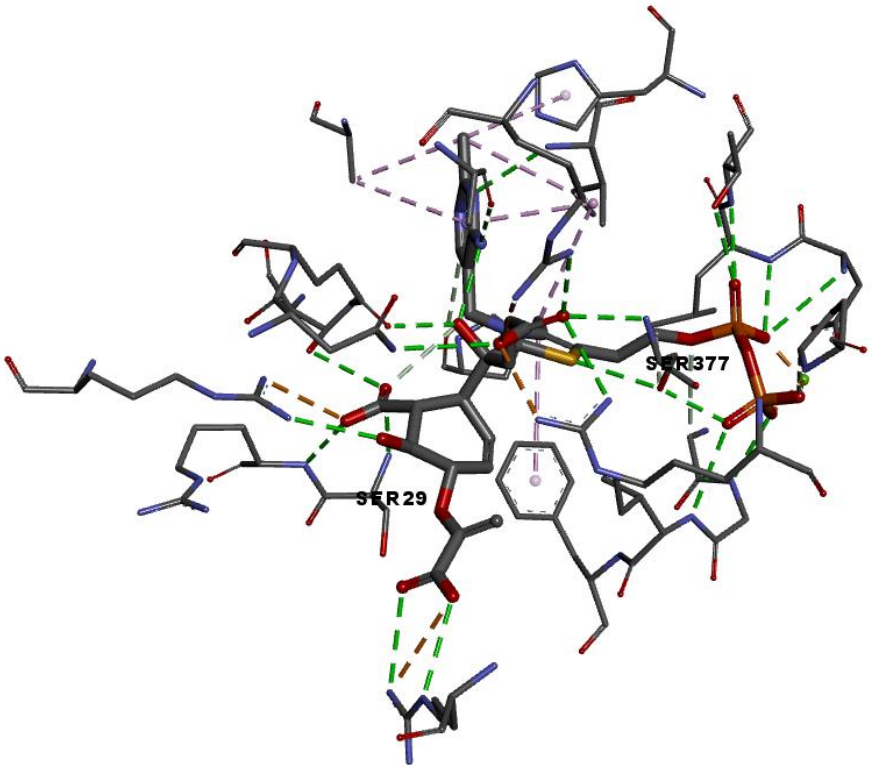

Figure 1. Crystal structure of the final intermediate in the MenD catalysed transformation of isochorismate.[2]

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Poster 7

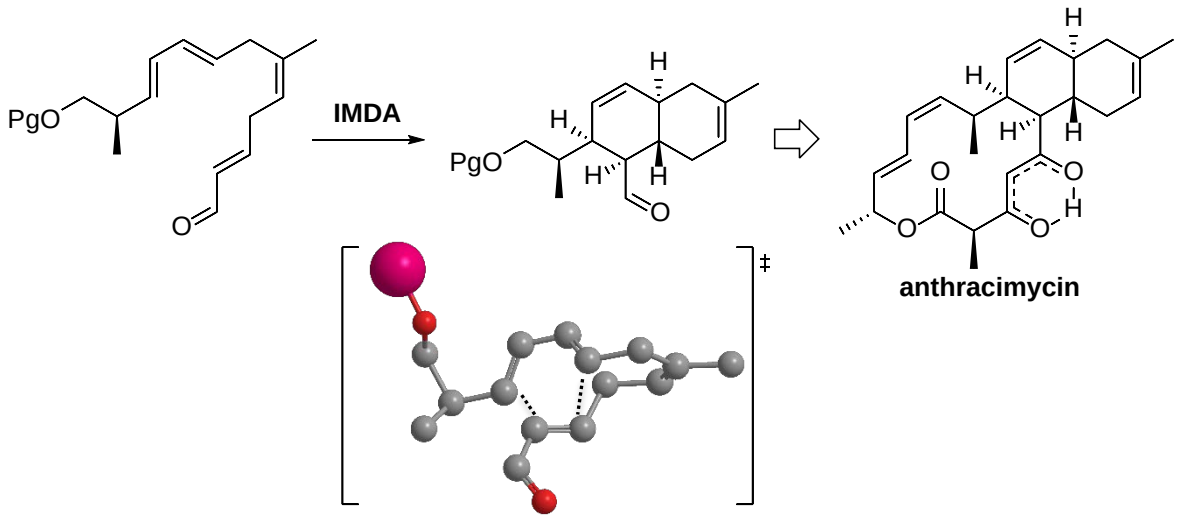
Synthesis and Biological Evaluation of the Potent Antibiotic Anthracimycin

Jared Freeman
Dr Daniel Furkert, Dist. Prof. Margaret Brimble

Antimicrobial resistance is a serious threat to humankind, and increasing incidence of methicillin-resistant *Staphylococcus aureus* (MRSA) infection represents both a global health and economic issue. [1] The discovery of novel compounds possessing antibiotic properties is critical to feed the pipeline for drug development. Macrocycles, consisting of a ring of 12 or more atoms, represent the middle ground between small molecule entities and biologics.[2] Macrocycles are gaining interest as drug candidates due to their favourable drug-like physicochemical and pharmacokinetic properties such as good solubility, lipophilicity, metabolic stability and bioavailability.[3]

Anthracimycin, a 14-membered macrocycle isolated in 2013,[4] is active against a panel of important drug-resistant bacterial strains, including *MRSA* (MIC 0.063 mg L^{-1}) and *Bacillus anthracis* (MIC 0.03 mg L^{-1}).[5]

This work aims to synthesise anthracimycin and structural analogues to elucidate its mechanism of action and establish the active pharmacophore. An intramolecular Diels-Alder cycloaddition (IMDA) will be used as a key reaction to furnish the decalin ring system. The complex molecular architecture, promising biological activity and unknown mode of action makes anthracimycin an interesting target for chemical synthesis and poses a unique chemical scaffold for drug discovery.



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Poster 8

Stability and Reliability of Gold Electrodes Probed with Various Faradaic Redox Species and a Non-Faradaic electrolyte for Biosensing Applications

Roshan Khadka[1]
Nihan Aydemir[1], Paul Baek[1], Andrew Kralicek[2], Jadranka Travas-Sejdic[1*]
[2]*The New Zealand Institute for Plant & Food Research Limited, Private Bag 92169, Auckland 1142, New Zealand*

Recent studies reported that electrochemical impedance spectroscopy (EIS) measurements of gold electrodes using ferri/ferrocyanide redox probe showed non-repeatable signals; hence this electrode-electrolyte system was not recommended for characterizing various gold surface modifications.[1,2] In this work, we significantly extended upon these studies and investigated the stability and reliability of the gold electrodes under three different Faradaic redox probes and a non-Faradaic electrolyte, at different stages of a biosensor surface preparation. Hexaamine ruthenium (III)/(II) chloride ($[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$) as a cationic redox probe, potassium ferri/ferrocyanide $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ as an anionic redox probe and hydroquinone (H_2Q) as a neutral redox probe were examined for Faradaic CV and EIS while Phosphate Buffer Saline (PBS) was used as an electrolyte for non-faradaic EIS and CV experiments. CV and EIS measurements of bare gold electrodes, after modification with the self-assembled monolayer (SAM) of 6-mercaptohexanoic acid (MHA) and after activation with standard N-hydroxysuccinimide (NHS)/1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide) (EDC) chemistry were conducted at different time intervals to confirm the reversibility and reproducibility of measured signals within the time frame of our need. Among the four investigated electrolyte systems, $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)^6]^{2+}$ and PBS buffer without any redox species showed very stable cyclic voltammograms and impedance spectra even after longer time periods. $[Fe(CN)_6]^{3-}/[Fe\ (CN)_6]^{4-}$ and H_2Q redox probes revealed variable and irreversible signals at the time scale of our measurement. AFM images confirmed the changes in surface morphology and roughness after treatment with these Faradaic redox probes and non-faradaic electrolyte, corresponding to the variable electrochemical signals observed. Hence, it is highly recommended to use hexaammineruthenium complex as the faradaic probe and PBS buffer as the non-faradaic medium with gold electrodes during CV and EIS in aqueous solutions in monitoring the electrode surface properties for biosensing applications.

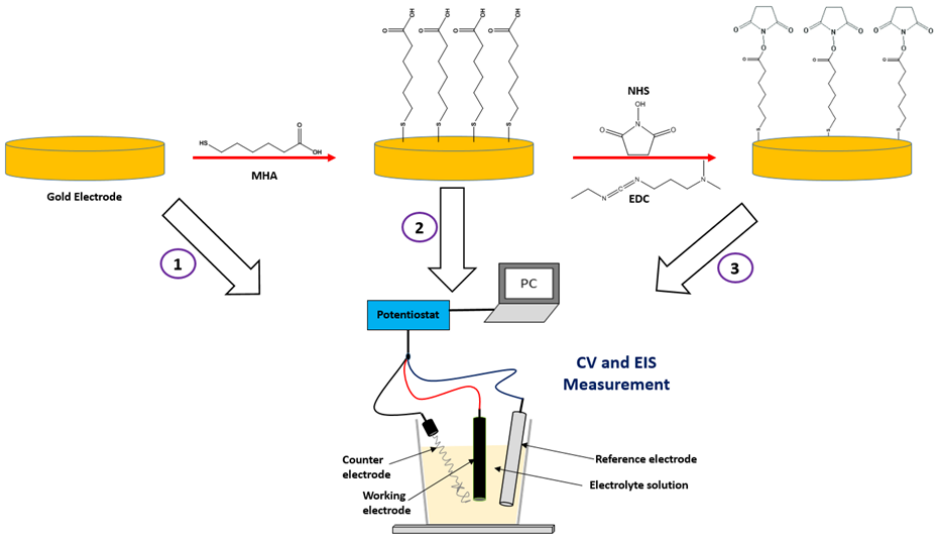

Figure 1. Stepwise surface modifications of a gold electrode suitable for chemical and biological sensing and electrochemical measurements at each step.

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Poster 9

Synthetic studies towards pseudocerosine

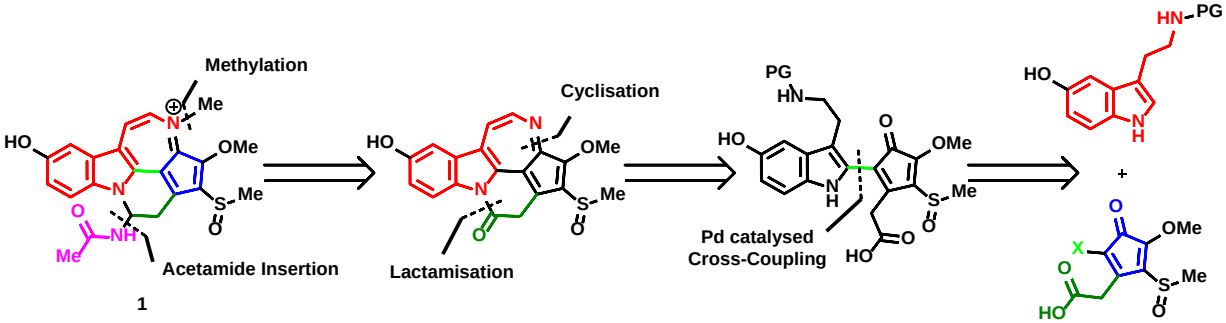
Se Hun Kim
A/Prof. Jonathan Sperry

Pseudocerosine (**1**) is the pigment responsible for the intense blue outer rim of the marine flatworm *Pseudoceros indicus*, which is found in the mangrove forests of small islands in western Pacific Ocean.[1] Structure elucidation of pseudocerosine has been reported in 2009, which describe the natural product as an indolic azafulvene alkaloid.[2]

To the best of our knowledge the heteroaromatic scaffold of **1** is novel. The structural novelty is within the exocyclic *N*-bearing azafulvene moiety which is flanked by an uncommon 2,3-azepinoindole. To date, pseudocerosine is known to exhibit mild cyctotoxicity against a human adenocarcinoma cell line (SKOV-3) with an IC_{50} value of 25 μM.[1]

From an evolutionary perspective we believe that pseudocerosine is a rather very complex scaffold for a marine organism to biosynthesise for pigmentation as a primary defence mechanism against predators. It is likely that that pseudocerocine may also exhibit a secondary mechanism such as a pheromone or possess inhibitory activity to deter predation. With no reported synthesis of pseudocerosine to date, its complex polycyclic heteroaromatic architecture, unknown mode of action and unique biosynthetic pathway makes pseudocerosine an interesting target for drug discovery and the development of new synthetic methodology.

Figure 1. Marine flatworm *Pseudocerosine indicus*.[1]



Scheme 1. Retrosynthetic analysis of pseudocerosine (**1**).

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Poster 10

Fundamental studies of polymer structure and their gas separation performances via synthetic approaches

Chao Liang
Professor Paul Kilmartin, Dr Jianyong Jin

The separation of gases with membranes[1] offers a number of advantages such as low energy use, relatively simple production equipment and less capital investment cost for industry. As a result, the membrane science and technology is one of the fastest growing branch both in scientific areas and industrial fields[2]. As well known, the efficiency of gas transport prosperities[3] in polymer membranes strongly depends upon the fundamental structure of the polymer. To estimate and reveal the correlation of polymer structure and their gas transport performance is an urgent requirement for new polymer design and synthesis.

In our research, polymers of intrinsic microporosity are used as a model membrane to investigate the correlation of polymer structure and their gas separation performance. Some synthesis strategies were explored. Meanwhile the relationship among the rigidity of monomer structure, the shape of polymer chain, and their gas separation performance were studied. Furthermore, in order to quantitatively understand the correlation of polymer structure and their gas separation performance, some molecular simulation methods are performed to characterize the structural and gas separation properties of polymer.

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Poster 11

Derivatisation of polyphenolic flavonoids extracted from fruits and vegetables

Stephen Lo

A/Prof. David Barker and Dr. Bruno Fedrizzi

Flavonoids are a large class of secondary metabolites found in plants and have a core structure consisting of the 15 carbon (C6-C3-C6) skeleton (**Figure 1**). Flavonoids are abundantly found in fruits and vegetables.[1] They contain multiple hydroxyl groups positioned in the A and B ring, and therefore are labelled as polyphenol compounds.

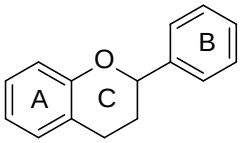
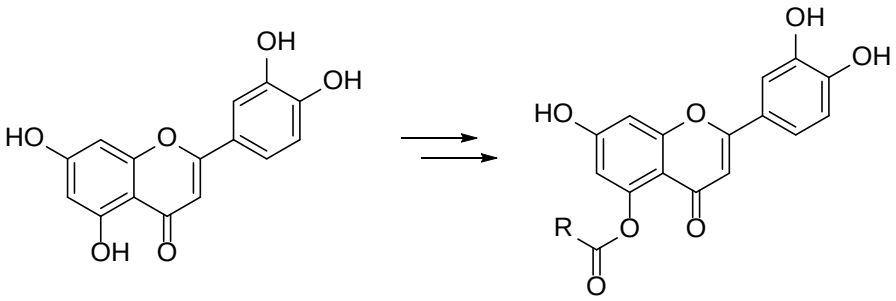


Figure 1. Flavonoid core C6-C3-C6 structure

Polyphenolic flavonoids exhibit a number of *in vitro* biological activity. They are particularly well known for their anti-oxidant activity.[2] They also display potential anti-inflammatory, antiproliferative, antimicrobial, neuroprotective and cardioprotective effects.[2,3] However, their *in vivo* therapeutic effects are significantly hindered by low bioavailability.[4] The derivatisation of these flavonoids can alter physicochemical properties of these compounds to help improve bioavailability. This allows the compound to effectively reach biological targets from site of administration and exert the desired therapeutic effects.

Since certain hydroxyl sites of these flavonoids contribute to bioactivity, this project aims to selectively derivatise hydroxyl sites of flavonoid compounds.[5] This will potentially improve bioavailability of the compounds as well as retain key hydroxyl sites to exert desired biological effects. Currently, the derivatisation of the flavonoid compound, luteolin, has been successful (**Scheme 1**).



Scheme 1. Derivatisation of the 5-hydroxy site of luteolin

Each of the synthesised flavonoid derivatives will then be subject to physicochemical and bioactivity studies. This will determine the one(s) with the best balance between good bioavailability and bioactivity, which will be more suitable as therapeutic candidates.

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Poster 12

New Solid State Materials for Gas Sensing and electronic applications

Ziqi Lu
Prof. Penelope J. Brothers; Prof. David E. Williams; Dr. David C. Ware

Semiconductors are well-known materials which can be used as gas sensors and many studies have showed that semiconducting metal oxides can be utilized as sensitive gas sensors (Figure 1).[1] Although it has been reported that these semiconducting metal oxide gas sensors show high sensitivity to combustible gases, their selectivity are limited. Furthermore, these sensors could be interfered by water vapour, lose sensitivity over time and require high working temperatures.[2]
Tin oxides (SnO_2) is a kind of semiconducting metal oxides which can be utilized as gas sensor (Figure 2). The highly porous structure of SnO_2 gives rise to the high sensitivity to particular gases.[2] However, it usually has a high resistivity and requires a high working temperature over 300℃.[1]
This project will try to use metal-doping and metal-decorating methods to enrich the surface structure of SnO_2 in order to increase its selectivity. Moreover, dopant metals could decrease the resistivity of SnO_2 dramatically and might reduce the required working temperature. This project aims to create new solid state gas sensing materials which are supposed to be stable, reliable, and low-cost and can be used at the lower working temperature.

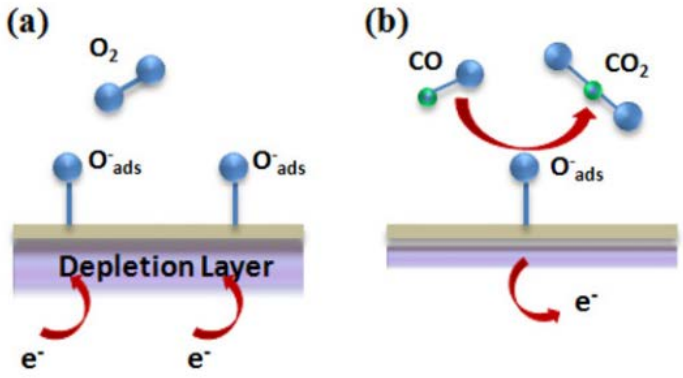

Figure 1. Illustration of *n*-type semiconductors: (a) adsorbed oxygen (b) reducing gases released.[3]

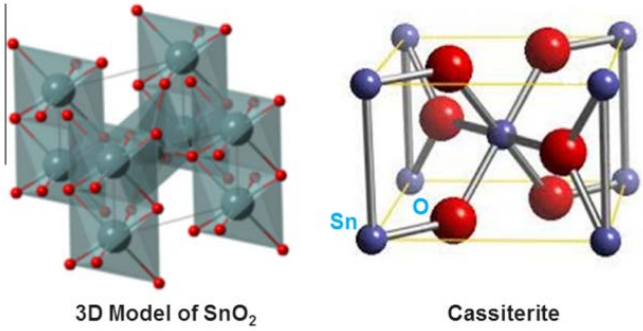

Figure 2. 3D model of tin oxides (SnO_2).[4]

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Poster 13

Citrate-ion Assisted Mineralization of Iron oxide Nanoparticles in Peroxiredoxin

Sesha Manuguri.[1,2], Kyle Webster.[3], Juliet Gerrard.[2, 3], David Williams.[1, 2] and Jenny Malmström.[2, 4]

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[2]*MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand*
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The antioxidant protein, peroxiredoxin is a supramolecular protein that can form array of supramolecular assemblies.[1] In its ring form, the size of its core is 7 nm in diameter. A histidine functionalized core can be utilized to grow inorganic metal nanoparticles. In a biomimetic process inspired by biological sequestration mechanisms of siderophores a ring protein[2], peroxiredoxin was used as a size restrained container to grow iron oxide nanoparticles. By incubating histidine functionalized core peroxiredoxin with 800 molar excess of Fe^{2+} ions in the presence of citrate anions at pH 8, we succeeded in mineralizing the core with iron oxide nanoparticles. During the mineralization process, citrate ions played a crucial role in supressing the bulk precipitation of iron oxides outside the protein core. Inductively coupled plasma mass spectrometry (ICP-MS) confirmed the presence of iron of about 220 atoms/ring. Thus, formed nanoparticles were characterized using TEM, AFM and magnetic properties were measured using a SQUID.

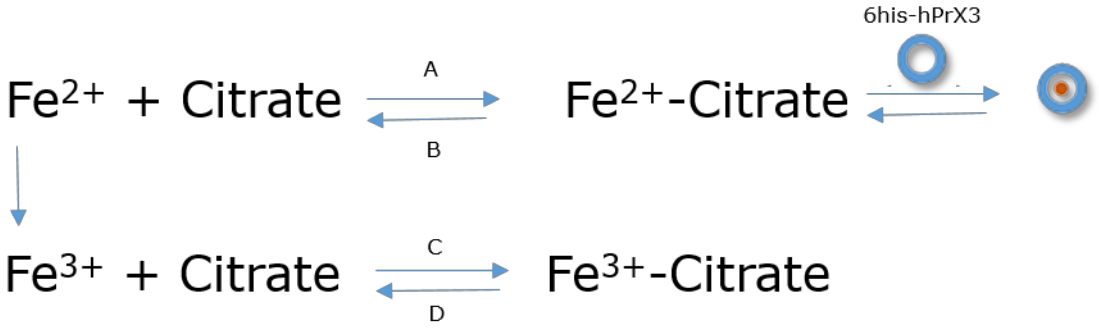

Figure 1. Plausible mechanism of iron binding to the protein in the presence of citrate. The blue ring symbolises the protein while the red circle symbolises the iron oxide nanoparticle formed.

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Poster 14

Effect of honey on growth and probiotic efficacy of *L. reuteri* DPC16

Anand Mohan
A/P Siew-Young Quek[1], Dr. Noemi Gutierrez-Maddox[2], Dr. Quan Shu[3]
[1]SCS, University of Auckland; [2]AUT University; [3]Bioactives Research New Zealand, Auckland, New Zealand

The potential prebiotic activity of some common Manuka honey varieties and an innovative blend incorporating probiotic fermentation metabolites (PFM) was evaluated by enumerating *Lactobacillus reuteri* DPC16 growth in UHT milk. Viability of the probiotic was significantly enhanced by 5% Manuka honey (UMF 18^{+} and MGO 550^{+}) in the synbiotic combinations assessed weekly over a period of four weeks (**Fig. 1**). Manuka honey blends supplemented with PFM, which are applied for their antibacterial properties against select pathogens, were also not inhibitory to the probiotic growth in UHT milk. The lactobacillus strain also demonstrated high tolerance to acid and bile salts after exposure for 1-1.5 hours. Interestingly, *L. reuteri* DPC16, which produces antimicrobial metabolites, and Manuka honey with established anti-bacterial activity can thus be utilised in promising synbiotic fermented product combinations. Further research on characterisation of the beneficial fermentation metabolites will be required to explore the mechanism of the antibacterial efficacy. The research contributes to establishing the prebiotic potential of Manuka honey and developing the less expensive blends containing antibacterial fermentation metabolites that can be equally effective.

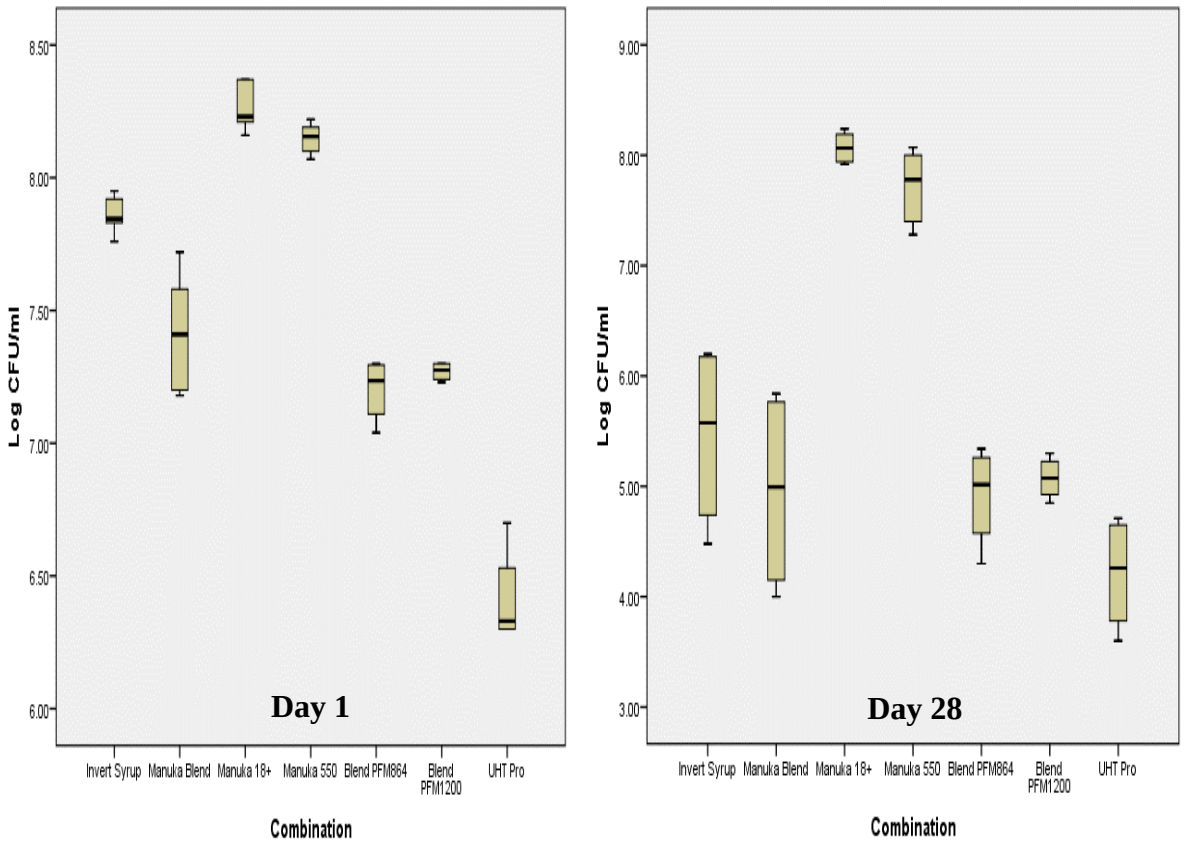

Figure 1. Total Viable Counts of *Lactobacillus reuteri* (DPC16) in UHT (Ultra-high-Temp) milk supplemented with different Manuka honey and blends containing probiotic fermentation metabolites (PFM).

Poster 15

Development of an electrochemical sensor to analyse uric acid in milk

Mahsa Motshakeri
Paul Kilmartin

Uric acid (UA) is one of the main contributors to the total antioxidant capacity of milk. It is not only an indicator of some serious diseases such as gout, hyperuricemia and Lesch-Nyhan syndrome, but also is a risk factor for leukaemia, pneumonia and cardiovascular disease[1]. Hence, it is of great importance to quantify UA in milk precisely in order to find a link between its concentration and diseases in cows and to profile milks for human consumption. The simplicity, low cost, rapidity and good selectivity of electrochemical procedures such as cyclic voltammetry make it feasible to detect antioxidants in plant extracts, blood plasma, tissue homogenates, wine, and particularly milk. Consequently, an electrochemical sensor was developed based upon the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) polymerized onto glassy carbon electrode in a propylene carbonate/$LiClO_4$ solution. Results showed good linear relationships between current intensities and UA concentrations in the range of 6 to 100 μM with sensitivity and detection limit (S/N = 3) of 0.87 × 10^{-3} μA μM^{-1} cm^{-2} and 6.5 μM, respectively. There was no interference from glucose or amino acids. This developed sensor was then successfully used for detection of UA in various milk samples with minimum interference from ascorbic acid.

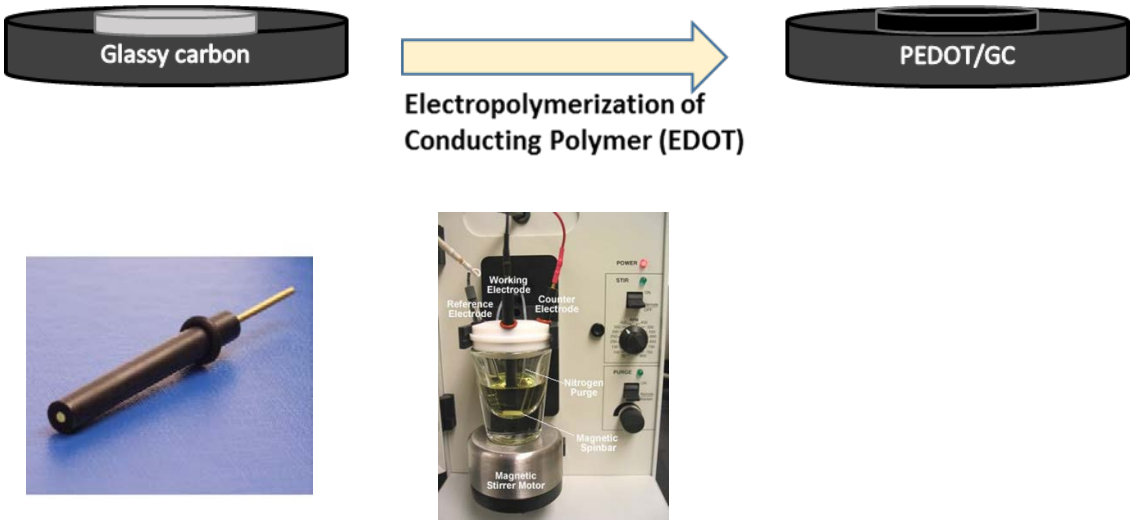

Figure 1. Electrodeposition of PEDOT on the glassy carbon electrode surface using cyclic voltammetry.

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Poster 16

Characterization of the key aroma compounds in different New Zealand grown feijoa cultivars

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Siew-Young Quek, Karen Bishop [1], Lynnette Ferguson [1]
[1] *Faculty of Medical and Health Sciences*

New Zealand has shown great interest in feijoa cultivation and marketing since 1983 [1]. It now has become a major feijoa growing and export country. As feijoa is becoming increasingly popular in recent years, one of the most important reasons is its lovely and unique aroma. Researchers have studied feijoa volatile compounds and found methyl benzoate and ethyl benzoate to be the main compounds [2, 3]. However, no existing study has revealed the compounds that contributes to feijoa aroma.

Although many feijoa cultivars are planted in New Zealand, namely Apollo, Unique and Opal Star, but very limited research has mentioned about feijoa cultivar differences especially in aroma. In this study, we initially employed headspace solid phase micro-extraction (SPME) combined with gas chromatograph-olfactory-mass spectrometry (GC-O-MS) to characterise the key aroma compounds in New Zealand grown feijoas. We also conducted essential oil extraction from peels and juice squeeze from fruits in order to better understand and further confirm the key aroma compounds. The aim of this study is to build up an aroma profile for feijoas, also in hoping to provide scientific evidence with feijoa cultivar selection.

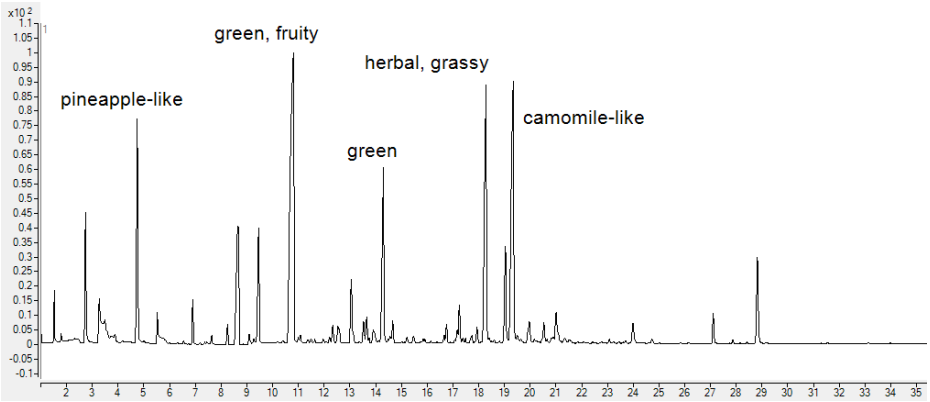

Figure 1. Some examples of aroma compounds in feijoa

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Poster 18

Benzimidazolium-derived *N*-heterocyclic carbene Ru^{II} and Os^{III} arene complexes and peptide conjugates as novel anticancer agents

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Cisplatin has long been renowned in the treatment of cancer. Intrinsic and acquired resistance to cisplatin as well as severe systemic toxicity[1] of the drug have spurred the search for new transition metal-based anticancer compounds.[2] Depending on the ligand of choice, organometallic compounds have shown promise, with 'piano-stool' complexes of the general formula [M(arene)(X)(Y)(Z)] having shown to be particularly efficacious and designable to be active against primary tumours or metastases.[3]

N-Heterocyclic carbenes (NHC) derived from an imidazolium scaffold result in a bioactive moiety when coordinated to ruthenium^{II}(arene) or osmium^{II}(arene) centres (**Figure 1a**). Thus, in the present work, ligands coordinated to the metal centre were varied to study the impact of symmetrical *N*-substituents, as well as the nature of anionic leaving group. Non-symmetrical NHCs were developed that upon conjugation to peptides would give metal-NHC-peptide complexes (**Figure 1b**) that are capable of targeting specific types of cancer. Conjugation was accomplished either through an acid linker between the NHC and the peptide or through NHCs bearing amino groups.

Biological evaluation has highlighted the cytotoxicity of selected symmetrical NHC Ru^{II} and Os^{II} complexes (numbers?) in the low to mid micromolar concentration range. These results highlight the promising potential of these complexes as novel anticancer agents.

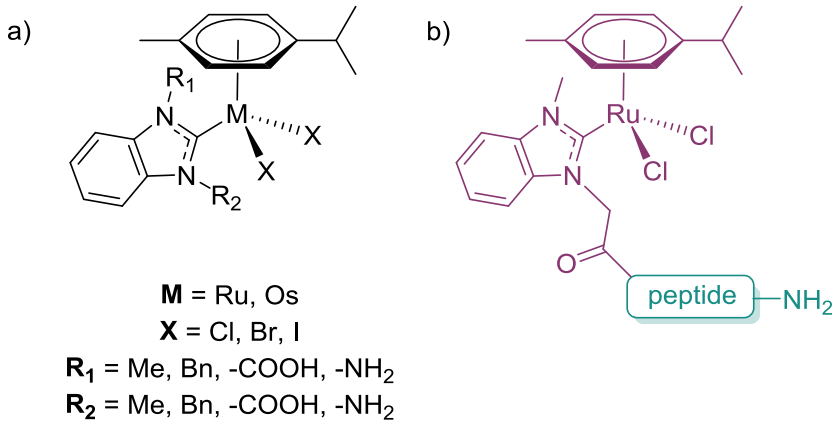

Figure 1. a) General structure of benzimidazolium-derived *N*-heterocyclic carbene Ru(II) and Os(II) arene complexes. b) General structure of metal-NHC-peptide conjugates.

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Poster 19

Self Assembly of peptides and proteins in five fold symmetry

Praveen George Vadakkedath
Ivanhoe K. H. Leung, Penny J. Brothers, Duncan J. McGillivray

The controlled organisation of peptides such as alpha helical peptides[1] and proteins is of increasing importance for different applications such as non-viral gene delivery, hydrogels, scaffolds for tissue engineering[1,2]. Among them, alpha-helical peptides are promising options for self assembly due to their diverse structure and function, and customisability[1,2]. They organize themselves into higher assemblies through covalent and non covalent interactions from short amino acid residues[3].

The main part of this work is to create five-fold symmetrical surface structures using peptides and proteins. In order to make five-fold symmetry, we need to understand other simple and common symmetric structures such as six-fold symmetry using peptides and proteins as building blocks. In our case, self assembly is based on the interaction of boronic acid with diols present in alpha-helical peptide which connect two peptides through boronic ester formation. The Boronic ester is reversible and is dependent on pH[4]. Through this linkage, we are trying to create six fold symmetric structures in solution. The Boronic ester formation is observed from NMR which will be supported by Mass spectroscopy. Further, the morphology of self assembled structure would be studied using CryoEM followed by degree of order using SAXS and SANS techniques.

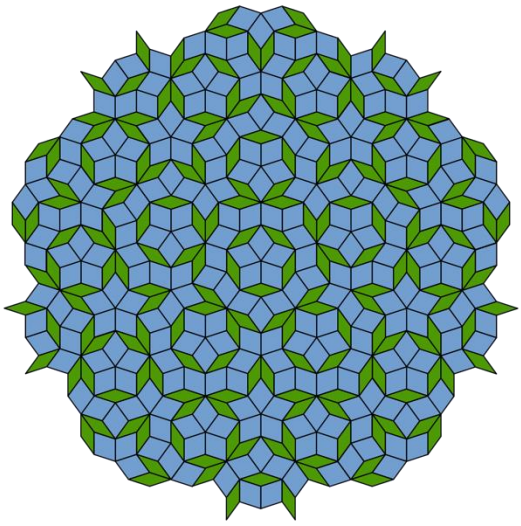

Figure 1. Two dimensional Penrose Tiling[5]

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Poster 20

Total Synthesis and Biological Evaluation of a New Lanthipeptide, Tikitericin

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Dist. Prof. Margaret Brimble, Dr. Paul W. R. Harris, Dr. Robert Keyzers[1]
[1]*School of Chemical & Physical Sciences, Victoria University of Wellington, New Zealand.*

Lanthipeptides are a group of structurally unique polycyclic peptides produced by bacteria, clearly distinguishable amongst the bacterial peptide toxins by their intramolecular thioether linked amino acids, lanthionine (Lan) or methyllanthionine (MeLan) (Figure 1).[1] Over 100 molecules sharing the (Me)Lan chemical motif have been reported, many of which exhibit antimicrobial activity and are referred to as lantibiotics.[2,3] Recently, a newly described but unpublished lanthipeptide tikitericin, was isolated from the New Zealand extremophilic microorganism *Thermogemmatispora* strain T81, collected at Tikitere (Hell's Gate), Rotorua.[4] Due to confidentiality reasons, the structure of tikitericin is not disclosed. However, nisin, a structurally similar lanthipeptide and commercially available lantibiotic is shown below (Figure 1). Tikitericin is highly likely to exhibit enhanced thermal and chemical stability (being sourced from an acidophile/thermophile) and bioactivity against Gram positive bacteria, however, due to the limited amount of natural product isolated this remains to be established. In order to analyse the chemical stability of the synthetic material under acidic and/or thermal stresses to assess any enhanced properties imbued by its structure, and to provide enough pure material for comprehensive bioassay profiling, we herein report the first total synthesis of tikitericin using a combination of organic and solid-phase peptide synthesis (SPPS).

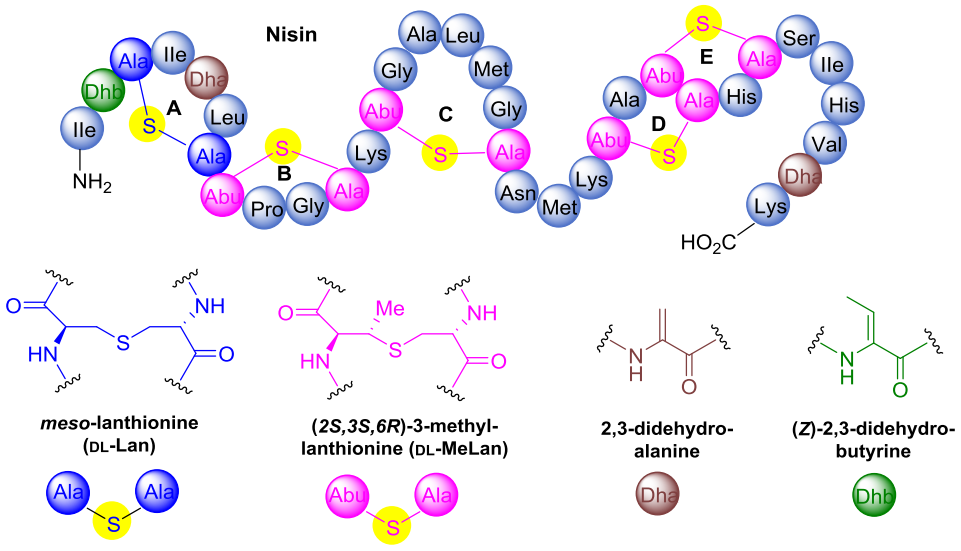

Figure 1. Sequence and ring topologies of nisin and chemical structures of its unusual amino acids.

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4. Dr Matt Stott (Extremophiles Research Group, GNS Science, Wairakei)

Poster 21

Synthesis of analogues of anti-tuberculosis peptide Calpinactam

Sutharsana Yathursan
Hannah Read[1], Siouxsie Wiles[1], Vijayalekshmi Sarojini
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The hexapeptide calpinactam, isolated from *Mortierella alpina* FKI-4905, has shown potential selective growth inhibition of *M. smegmatis* and *M. tuberculosis* with the MIC values 0.78 and 12.5 µg/ml respectively[1-3]. Therefore, two analogues of calpinactam were designed to achieve greater *in-vivo* stability and improved biological activity, by replacing the calpinactam ring with unnatural amino acids 1-aminocycloheptane-1-carboxylic acid (Ac7c) and α,α-di-n-propylglycine (dpg). The syntheses, characterization and *in-vitro* antimicrobial activity including anti-mycobacterial activity of these peptides conducted using the bioluminescence assay[5] will be presented.

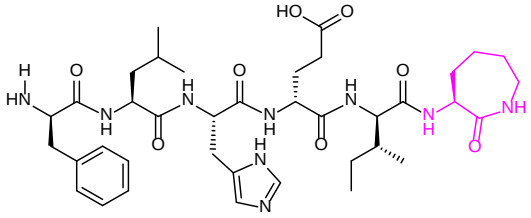

Figure 1. Chemical structures of calpinactam

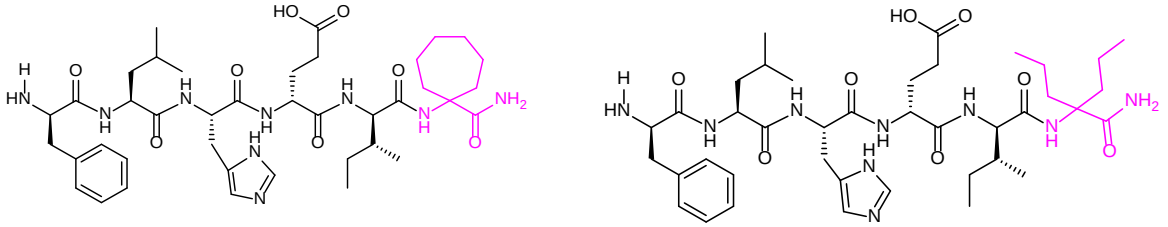

Figure 2. Chemical structures of calpinactam analogues; Ac7c analogue and Dpg analogue

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Poster 22

Plasmonic Enhanced Visible-light Driven Photocatalysts for Solar Hydrogen Production

Piao Ye
Supervisors: Geoffrey Waterhouse; Dongxiao Sun-Waterhouse

Photocatalysts-driven solar water splitting has drawn much interest across the scientific community because it is a promising way to transfer the costless solar energy into the clean and renewable energy carrier H_2.[1] Among several semiconductors whose bandgap sandwiches the hydrogen evolution half reaction potentials in water splitting, TiO_2 is particularly widely used as photocatalyst for this process due to its stability, nontoxicity and low cost. Though the large bandgap (3 - 3.2 eV) of TiO_2 makes it a good absorber of ultraviolet light, it is immune to visible light, which takes up to 40% in the solar emission. Rapid recombination of photogenerated electron-hole pairs in the body of TiO_2 photoanode also decreases hydrogen production efficiency. In recent years a new approach that exploits localized surface plasmon resonance (LSPR) in metal nanostructures to enhance photoactivity of TiO_2 has been extensively investigated.[2-4] We aim to contribute to the field of plasmonic enhanced visible-light driven photocatalytic solar hydrogen production by exploring LSPR in gold nanorods(AuNRs) and incorporating them with TiO_2 substrates to form high-performance photocatalysts. Efficiency of water splitting is measured in a three-electrode photoelectrochemical(PEC) cell where our AuNR/TiO_2 samples work as a photoanode.

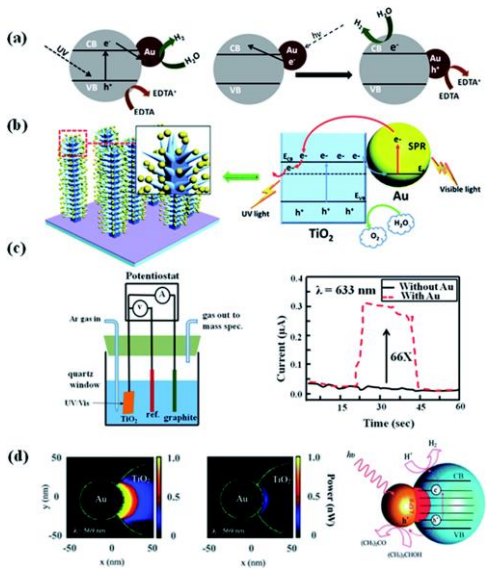

Figure 1. (a) & (b) Schematic representation for the proposed rationalization of the photocatalytic activity of Au/TiO_2 under UV light and visible light excitation based on the electron transfer mechanism. (c) The design of photoelectrochemical cell and the photocurrent of anodic TiO_2 without or with Au NPs at zero bias voltage upon the irradiation with visible light. (d) Simulated optical-absorption maps of Janus Au 50 nm–TiO_2 nanostructures. The scheme shows the proposed mechanism for LSPR enhanced photocatalytic hydrogen generation in these nanostructures.[5]

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Poster 23

Syntheses of antimicrobial peptides using CLipPA technology

Victor Yim
Dist. Prof. Margaret Brimble, Jianyong Jin, *Simon Swift*[a]
[a] Faculty of Medical and Health Sciences

The rhizosphere is a small zone in the soil surrounding the plant roots.[1] The roots provide nutrients to surrounding microbiota in the form of sugars, amino acids and root border cells into the rhizosphere. Some microbes excrete metabolites known as non-ribosomally biosynthesised peptides (NRPs).[2] They exhibit antimicrobial activities, thereby killing microbes competing for the same source of nutrients. NRPs are structurally diverse and serve as a great source for the discovery of novel natural structures. Among these are the antifungal iturin family[3] and the antibacterial battacin[4], both of which are lipopeptides (Figure 1).

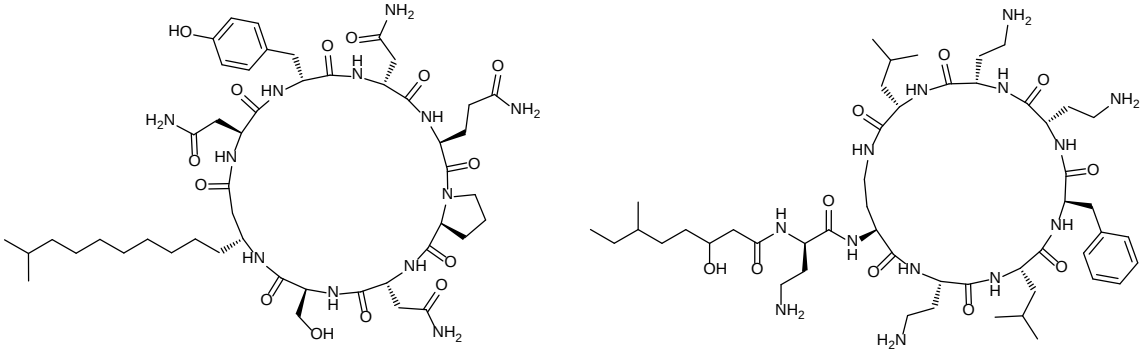
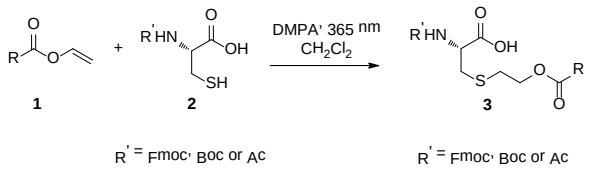


Figure 1. Structures of lipopeptides iturin A (left) and battacin (right)

Lipopeptides can be chemically accessed with the technique known as '**C**ysteine **Lip**idation on a **P**eptide or **A**mino acid' (CLipPA).[5] A variety of vinyl esters **1** is reacted with N^{α}-protected cysteine **2** to generate a library of cysteine derived lipoamino acids **3** (Scheme 1). These form the building blocks that were incorporated into the syntheses of lipopeptides mimics. CLipPA circumvents conventionally difficult or time-consuming methods of synthesising lipid building blocks.[6,7] The bioactivity of CLipPA analogues of iturins and battacin will be evaluated against plant pathogenic microbes.



Scheme 1. General CLipPA reaction between vinyl ester **1** and N^{α}-protected cysteine **2** to give CLipPA product **3**

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Poster 24

Direct Writing of 3D Conducting Polymer Arrays for Biological Cell Sensing

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Direct writing has been proven to be an effective and versatile method for 3D fabrication of conducting polymer structures. It provides a precisely localized and highly controllable microfabrication technique[1]. 3D conducting polymer micro arrays produced by this approach have various possibilities and great potential combining with biological cells.

Herein we demonstrate the 3D writing of high aspect ratio conducting polymer wires by the Scanning Ion Conductance Microscope (SICM). Writings of conducting polymers with various formulations (different concentration of organic solvents and cross-linking agents) were realised. Organic solvents treatments as well as the cross-linking agent contribute to a significantly enhanced water-stability, which is critical for most biological applications.

SEM and Raman were used for surface morphology and polymer structure characterization. These CP wires have smooth surface and can reach a very wide range of aspect ratios. Localised measurements of electrochemical activity between wires with different length have been compared. The results indicate that they all possess good electrical and electrochemical properties. Furthermore, these pillars have fantastic mechanical properties. They exhibits extraordinary robustness, elasticity and flexibility. All these properties bring a good prospect for the applications of the direct written 3D conducting polymer micro structures as functional biological sensors.

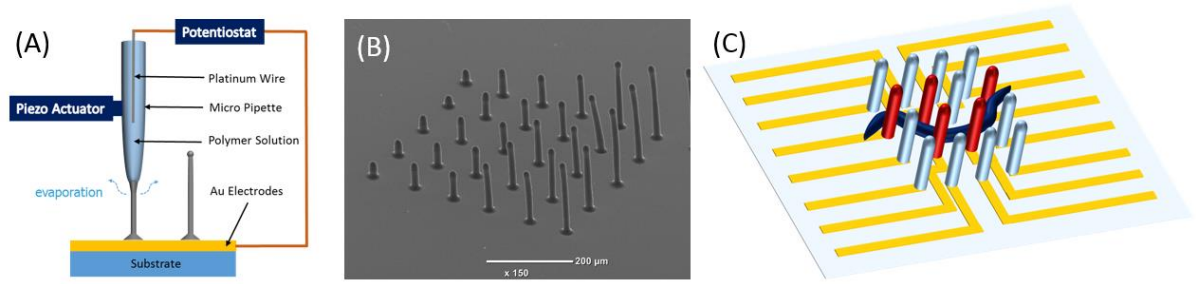

Figure 1. (A) Schematic mechanism of direct writing. (B) SEM of CP array. (C) Applications of CP arrays for C.elegans sensing and stimulation[2].

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Poster 25

Development of Y_2O_3:Eu@SiO_2 Phosphors for White LED Application

Huihua Zhou
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White light-emitting diodes (LEDs) are widely expected to replace incandescent bulbs and fluorescence lamps for domestic and commercial lighting in the near future. Currently, white LEDs are produced by coating blue emitting semiconductor chip with a yellow phosphor, or by coating UV emitting chips with red-green-blue (RGB) phosphors. Eu^{3+}-doped yttria (Y_2O_3:Eu) is an efficient red-emitting phosphor, currently used with UV-pumped LEDs.[1] Eu^{3+} is one of the most effective trivalent rare earth activators,[2] whilst Y_2O_3 is a suitable host material because of its low background emission and excellent chemical stability under vacuum environment. Conventionally, Y_2O_3:Eu is synthesized by high-temperature solid state reaction. The reaction process is relatively simple and easily to be commercialized. However, this method has following drawbacks: (1) high calcination temperatures up to 1600 ^oC and long reaction times (2) need for reducing gases such H_2 in the high temperature environment (3) tendency of cluster formation in products. Sol-gel routes offer promising alternative approaches towards rare earth doped phosphors. Sol-gel routes allow the large scale production of nano-sized phosphors particles with high purity at low temperatures (e.g. 500-800 ^oC). Here, sol-gel method is used to produce phosphors with a core (SiO_2)-shell (Eu:Y_2O_3) structure.

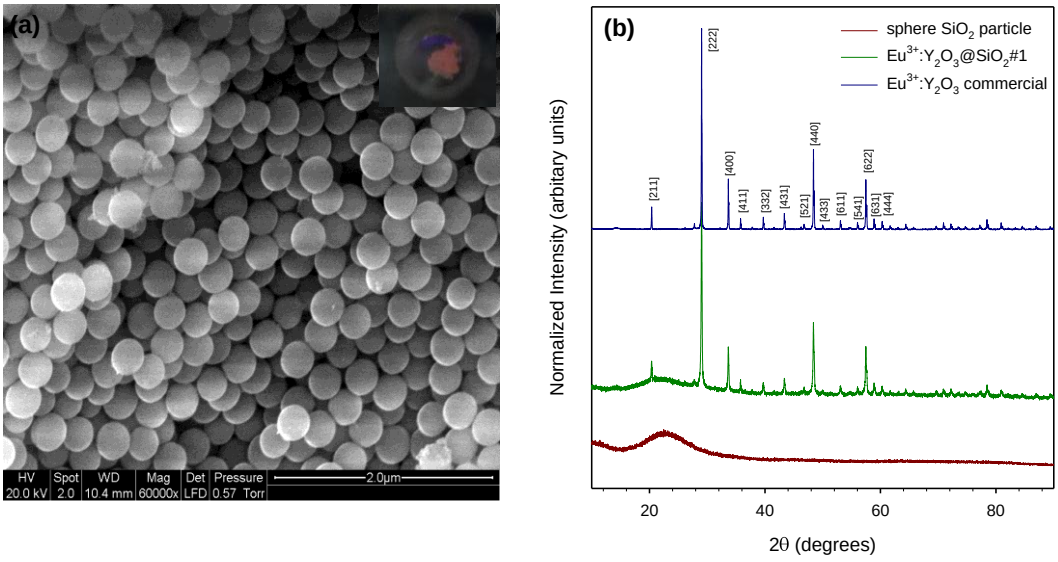

Figure 1. (a) SEM image of the Eu:Y_2O_3@SiO_2. The inset shows the luminescence of Eu:Y_2O_3@SiO_2 under 365 nm excitation (b) XRD data for the SiO_2 core, Eu:Y_2O_3@SiO_2 and a commercially available Eu:Y_2O_3 powder.

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Poster 26

Investigation on the delivery of vision-beneficial multi-micronutrients for effective absorption

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Fish oils contain long-chain polyunsaturated fatty acids, also known as omega-3 fatty acids, which are deemed to be associated with eye development and health. In addition, β-Carotene, lutein and zeaxanthin are the three of the most widely applied carotenoids as either food colorants or functional nutraceuticals. They are known for a broad variety of biological activities including vision protection[1]. However, due to the sensitives of omega-3 fatty acids as well as carotenoids to air, heat and light, there is obviously a need to develop a delivery system for these important nutrients against oxidation and decomposition. Microencapsulation is a technology by which food ingredients or bioactive components are coated with or entrapped with another polymer matrix. Microencapsulation with a mono-disperse droplet spray dryer is a novel technique introduced to generate uniform micro-particle products. Compared to conventional spray drying, the mono-disperse droplet spray dryer is capable of producing mono-disperse droplets and more defined drying history of the droplets to obtain uniform particles[2]. To better study the bioavailability of microcapsules coating with multi-micronutrients, it is quite necessary to explore their digestion and absorption behaviour with *in vitro* simulation experiment.

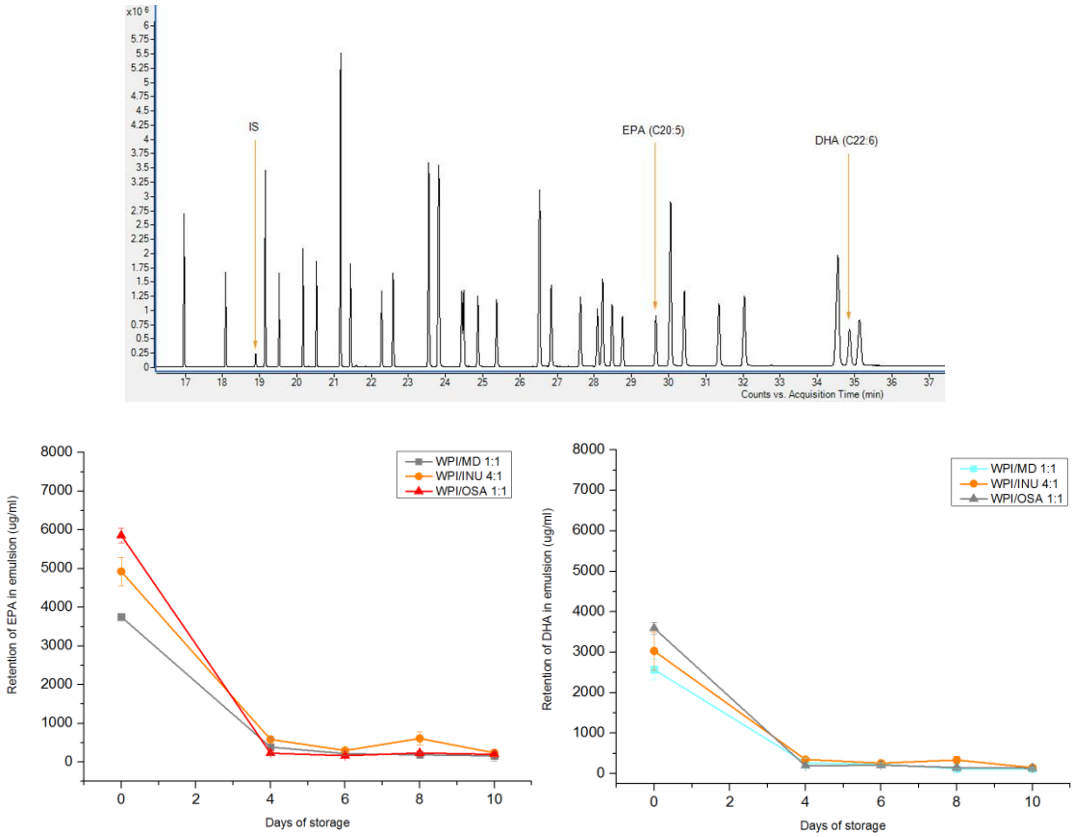

Figure 1. The chromatogram of EPA and DHA, and retention of EPA (C20:5), DHA (C22:6) in emulsion during a 10 days accelerated storage trial at 37℃.

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