2\textsuperscript{nd} Queensland Annual Chemistry Symposium
QACS 2017

Monday 27\textsuperscript{th} November 2017
8:30am – 5:30pm

Queensland University of Technology
Gardens Point Campus
George Street, Brisbane, Queensland, Australia

Programme

A copy of this programme and abstracts will also available online at

The organising committee:
Assoc Prof John McMurtrie (Chair) ▪ Dr Christiane Lang (Treasurer)
Prof Godwin Ayoko ▪ Assoc Prof Leonie Barner ▪ Assoc Prof Sarah Cresswell
Lukas Michalek ▪ Dr Laleh Moghaddam ▪ Hendrik Woehlk
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## Morning Programme

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<td>Opening remarks</td>
<td>John McMurtrie</td>
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<tr>
<td>8:50</td>
<td><strong>Plenary lecture P1:</strong> Chemical probes to Answer Fundamental Biological Questions</td>
<td>Sally-Ann Poulsen</td>
<td>Z406</td>
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<td>9:30</td>
<td><strong>Plenary lecture P2:</strong> Mitigating the effects of the toxin simplexin in Pimelea poisoning of cattle</td>
<td>Mary Fletcher</td>
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<tr>
<td>10:10</td>
<td>Morning tea</td>
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### Morning Parallel Sessions

#### Organic and Medicinal Chemistry - Chair: Lewis Chambers

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<tr>
<td>10:30</td>
<td>A1</td>
<td>Amino acid based anti-biofilm compounds</td>
<td>Jessica Harris</td>
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<tr>
<td>10:45</td>
<td>A2</td>
<td>Design, synthesis and biological evaluation of uridine-peptide conjugates as bisubstrate analogue inhibitors of human O-GlcNAc transferase (OGT)</td>
<td>Philip Ryan</td>
</tr>
<tr>
<td>11:00</td>
<td>A3</td>
<td>Structure function relationships of a ribityl uracil antigen on T-cell activation</td>
<td>Geraldine Ler</td>
</tr>
<tr>
<td>11:15</td>
<td>A4</td>
<td>Synthesis of iminosugar uronidase inhibitors as potential pharmacological chaperones for MPS I and MPS VII</td>
<td>Gareth Doherty</td>
</tr>
<tr>
<td>11:30</td>
<td>A5</td>
<td>Selective ARTD8 Inhibitors as a potential late stage prostate cancer treatment</td>
<td>Amanda Tauber</td>
</tr>
<tr>
<td>11:45</td>
<td>A6</td>
<td>Development of bicyclic nitroimidazoles as antitubercular and antiparasitic agents</td>
<td>Chee Wei Ang</td>
</tr>
<tr>
<td>12:00</td>
<td>A7</td>
<td>Design, Synthesis and Biological Evaluation of Chemical Probes for Visualising DNA Synthesis in Proliferating Cells</td>
<td>David Hilko</td>
</tr>
<tr>
<td>12:15</td>
<td>A8</td>
<td>How reliable are the structural models used in drug design?</td>
<td>Nicole Wheatley</td>
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#### Natural Products, Analytical and Theoretical Chemistry - Chairs: Michele Prinsep

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<tbody>
<tr>
<td>10:30</td>
<td>B1</td>
<td>A reusable nanostructured substrate for the selective detection of Pb(II) ions</td>
<td>Daniel Sarfo</td>
</tr>
<tr>
<td>10:45</td>
<td>B2</td>
<td>Can wastewater-based epidemiology be used for the assessment of anabolic steroid use?</td>
<td>Katja Shimko</td>
</tr>
<tr>
<td>11:00</td>
<td>B3</td>
<td>Active metal template synthesis of a switchable [2]rotaxane in solution and on the surface</td>
<td>Sean Hewson</td>
</tr>
<tr>
<td>11:15</td>
<td>B4</td>
<td>Phytates and oxalates in Kakadu plum (Terminalia ferdinandiana): Toxins to be considered</td>
<td>Saleha Akter</td>
</tr>
<tr>
<td>11:30</td>
<td>B5</td>
<td>2D C3 Marfey's method for amino acid analysis and structure elucidation in peptidic natural products</td>
<td>Krishantha Wardamune Gedara</td>
</tr>
<tr>
<td>11:45</td>
<td>B6</td>
<td>Something new in Hartree-Fock theory</td>
<td>Tim Gould</td>
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<tr>
<td>12:00</td>
<td>B7</td>
<td>A reaction pathway bifurcation in the (4+3)-cycloaddition</td>
<td>Jed Burns</td>
</tr>
<tr>
<td>12:15</td>
<td>B8</td>
<td>Quantification of excipients in nutraceuticals using FTIR ATR and hand-held Raman; preliminary results</td>
<td>Godfred Duodu</td>
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### Inorganic and Polymer Chemistry - Chair: Rafael da Silva Rodrigues

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<tr>
<td>10:30</td>
<td>C1</td>
<td>Jacob Whittaker</td>
<td>Assembly of a M₄L₆ tetrahedron from a multidentate organic ligand</td>
</tr>
<tr>
<td>10:45</td>
<td>C2</td>
<td>Bowie Soon Ket Chong</td>
<td>Emissive lanthanide complexes based on pyridyl-8-hydroxy-quinoline chelates</td>
</tr>
<tr>
<td>11:00</td>
<td>C3</td>
<td>Lukas Michalek</td>
<td>Polymer on Top: Current limits and future perspectives of quantitatively evaluating surface grafting</td>
</tr>
<tr>
<td>11:15</td>
<td>C4</td>
<td>Tenille Herd</td>
<td>Investigation of the fluorescence efficiency of profluorescent nitro oxide adducts via electrochemical processes</td>
</tr>
<tr>
<td>11:30</td>
<td>C5</td>
<td>Hydar Al-Fayaad</td>
<td>Design and synthesis of new chiral metal organic frameworks</td>
</tr>
<tr>
<td>11:45</td>
<td>C6</td>
<td>Thu Trang Do</td>
<td>Acceptors based on 1,8-naphthalimide and fluorenone building blocks for high efficiency fullerene-free organic solar cells</td>
</tr>
<tr>
<td>12:00</td>
<td>C7</td>
<td>Jongryul Park</td>
<td>Poly(2-oxazoline)-drug conjugate hydrogels as implantable drug delivery systems</td>
</tr>
<tr>
<td>12:15</td>
<td>C8</td>
<td>Johanna Kerber</td>
<td>pH-sensitive polymersomes as carrier for light-triggered encapsulation studies</td>
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<tr>
<td>12:00</td>
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<td>Lunch</td>
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## Afternoon Programme

### Organic and Medicinal Chemistry - Chair: Nicole Wheatley

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<th>Speaker</th>
<th>Title</th>
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<tr>
<td>1:30</td>
<td>A9C</td>
<td>Samantha Catt</td>
<td>Light-activated nitrile-imine mediated reaction pathways for bioink synthesis in biofabrication</td>
</tr>
<tr>
<td>1:35</td>
<td>A10C</td>
<td>Colin Schiemer</td>
<td>Chiral induction through halogen bonding</td>
</tr>
<tr>
<td>1:40</td>
<td>A11</td>
<td>Michael Netzel</td>
<td>Identification and quantification of dietary anthocyanins and metabolites in human urine</td>
</tr>
<tr>
<td>1:55</td>
<td>A12</td>
<td>Rhia Stone</td>
<td>Near-infrared fluorescent antibiotics for live cell and in vivo bacterial imaging</td>
</tr>
<tr>
<td>2:10</td>
<td>A13</td>
<td>Bhautikkumar Patel</td>
<td>Design, synthesis and biological evaluation of C-5 substituted uridine analogues by using solid-phase microwave-assisted ligand-free Suzuki-Miyaura cross-coupling reaction</td>
</tr>
<tr>
<td>2:25</td>
<td>A14</td>
<td>Sarah McGregor</td>
<td>Investigating the relationship between phase behaviour and photovoltaic performance</td>
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<tr>
<td>2:40</td>
<td>A15</td>
<td>Jan Philip Menzel</td>
<td>Wavelength dependence of light–induced cycloadditions</td>
</tr>
<tr>
<td>2:55</td>
<td>A16</td>
<td>Louise Forster</td>
<td>Looking into the mirror: A detailed investigation into nudibranch mimicry</td>
</tr>
<tr>
<td>3:10</td>
<td>A17</td>
<td>Qian Liu</td>
<td>Naphthalene flanked diketopyrrolopyrrole (DPPN): A new fused aromatic moiety for constructing high performance organic semiconductors</td>
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Venue: Z304

Venue: Z-Block Atrium
### Afternoon Parallel Sessions cont.

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<td>1:30</td>
<td><strong>Natural Products, Analytical and Theoretical Chemistry - Chair: Tim Gould</strong>&lt;br&gt;Venue: Z205</td>
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<tr>
<td>1:30</td>
<td>B9C Waleed Hassanain&lt;br&gt;<em>SERS nanosensor for the clinical diagnosis of brain injury biomarker</em></td>
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<tr>
<td>1:35</td>
<td>B10C Natasha Hungerford&lt;br&gt;<em>Pyrrolizidine alkaloids – Natural toxins risk in Queensland honey</em></td>
</tr>
<tr>
<td>1:40</td>
<td>B11 Rafael da Silva Rodrigues&lt;br&gt;<em>Dynamic covalent chemistry at the solution:surface interface</em></td>
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<td>1:55</td>
<td>B12 Osama Mohamed&lt;br&gt;<em>Chemical study of N-amino-l-proline methyl ester Schiff bases isolated from Fish-Gut derived fungus Beauveria sp.</em></td>
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<td>2:10</td>
<td>B13 Iftekhar Ahmed&lt;br&gt;<em>New flavonoids and saponins from Gynostemma pentaphyllum (Thunb.) Makino</em></td>
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<td>2:25</td>
<td>B14 Michele Prinsep&lt;br&gt;<em>Applications of liquid chromatography-mass spectrometry (LC-MS) to natural products explorations of New Zealand marine invertebrates.</em></td>
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<td>2:40</td>
<td>B15 Hung Trieu Hong&lt;br&gt;<em>Determination of pigments of purple sweetcorn using LC-PDA-MS/MS</em></td>
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<td>2:55</td>
<td>B16 Anh Dao Phan&lt;br&gt;<em>Assessing important polyphenols and organo-sulfur compounds in selected varieties of Australian grown onions using Orbitrap LC-ESI-MS analysis</em></td>
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<td>3:10</td>
<td>B17 Alfred Kwablah Anim&lt;br&gt;<em>Spatial assessment of some legacy POPs in estuarine sediment</em></td>
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<td>1:30</td>
<td><strong>Inorganic and Polymer Chemistry - Chair: Jenny Thu Trang Do</strong>&lt;br&gt;Venue: Z304</td>
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<td>1:30</td>
<td>C9C Andres Reyes&lt;br&gt;<em>Modulation of spin-crossover behaviour of Metal complexes encapsulated in halogen bonded networks</em></td>
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<tr>
<td>1:35</td>
<td>C10C Lewis Chambers&lt;br&gt;<em>Spatial control of self-assembly in photo-sensitive block copolymers</em></td>
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<td>1:40</td>
<td>C11 Jessica Bilyj&lt;br&gt;<em>Inducing high oxidation states in thiosemicarbazone complexes</em></td>
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<td>1:55</td>
<td>C12 Isaac Etchells&lt;br&gt;<em>The Influence of metal-metal distance and the mechanism of energy transfer in NIR luminescent bimetallic lanthanide ruthenium terpyridine complexes</em></td>
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<td>2:10</td>
<td>C13 Kasun Athukorala Arachchige&lt;br&gt;<em>Halogen Bonded Supramolecular Networks containing Nickel(II) and Copper(II) complexes</em></td>
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<td>2:25</td>
<td>C14 Md Abu Sayeed&lt;br&gt;<em>Electrocatalytic water oxidation at amorphous trimetallic oxides based on FeCoNiOx</em></td>
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<td>2:40</td>
<td>C15 Myles Atkinson&lt;br&gt;<em>A ligand field assessment of Ni(II) in ZnAl2O4 spinel</em></td>
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<tr>
<td>2:55</td>
<td>C16 Hong Duc Pham&lt;br&gt;<em>Novel and dopant-free anthanthrone dye-based organic hole transporting materials for cost efficient and highly performing perovskite solar cells</em></td>
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<tr>
<td>3:10</td>
<td>C17 Gabrielle Netzel&lt;br&gt;<em>Identification and quantification of indospicine and its metabolites in camel tissue using UHPLC-MS/MS</em></td>
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<td>3:25</td>
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### Afternoon Plenary Session - Chair: Leonie Barner<br>Venue: Z406

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<th>Time</th>
<th>Plenary Lecture P3: Nicole Rijs&lt;br&gt;<em>Deconstructing molecular catalysis and self-assembly by advanced mass spectrometry and ion mobility; towards rationally designed molecular reaction vessels</em></th>
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<td>3:50</td>
<td><strong>Presentation of Prizes for Contributed Talks and Short Presentations and Closing Remarks</strong>&lt;br&gt;Venue: Z-block Atrium</td>
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<td>3:50</td>
<td><strong>Plenary Lecture P4: Jerome Waser (2017 Davies Collison Cave Plenary Lecturer)</strong>&lt;br&gt;<em>Ring-Strain and Hypervalent Bonds: From Synthesis to Chemical Biology</em></td>
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<td>4:50</td>
<td><strong>The symposium will be followed by a social gathering to stimulate further networking opportunities at the Botanic Bar</strong></td>
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Chemical probes to answer fundamental biological questions

Sally-Ann Poul sen*

*Griffith Institute for Drug Discovery, Griffith University, Nathan Campus, Brisbane, QLD 4111
s.poul sen@griffith.edu.au

Chemical probes are small molecule reagents that have a profound impact on our ability to answer fundamental biological questions. This presentation will encompass several aspects of a wider program that involves the design and synthesis of chemical probes to either label or to partner with biomolecules of therapeutic interest.

A) The enzymes carbonic anhydrase are highly expressed in the hypoxic core of solid tumours, where they maintain the pH of the tumour microenvironment. As tumour pH is central to cancer cell survival, metastasis and drug resistance and this reliance has triggered a need to develop small molecules that selectively target carbonic anhydrases for use as chemical tools and/or as leads for therapeutic drug discovery. Medical imaging, fragment screening and photoaffinity probes targeting carbonic anhydrases will be discussed.

B) A common method of evaluating cellular proliferation is to label DNA with a metabolic chemical probe during the synthesis phase (S-phase) of the cell cycle during which time DNA is replicated. The design and synthesis of chemical probes for labelling DNA in mammalian and parasites will be discussed.

Overall this presentation will highlight research that aims to improve the interaction between chemical synthesis and the biological world.
Mitigating the effects of the toxin simplexin in *Pimelea* poisoning of cattle

Mary T. Fletcher

*Queensland Alliance for Agriculture and Food Innovation, University of Queensland, Health and Food Sciences Precinct Coopers Plains, QLD 4108  
mary.fletcher@uq.edu.au*

Simplexin is an unusual diterpenoid orthoester that occurs in native *Pimelea* plant species across arid inland grazing pastures of Australia, and is responsible for unique poisoning syndrome in cattle in these regions. This toxin acts in a number of ways, as both an intestinal irritant and also a protein kinase C activator. Animals effected by *Pimelea* poisoning show a range of symptoms from characteristic severe swelling of the head and neck (due to subcutaneous edema), emaciation, diarrhoea, lethargy and frequently death. The incidence of *Pimelea* poisoning is sporadic and contingent on prevalence of *Pimelea* plants, level of toxin and availability of other pasture. Analysis of simplexin levels in *Pimelea* plant material by liquid chromatography-tandem mass spectrometry (LC-MS/MS) has demonstrated that toxin levels are dependent on *Pimelea* species, growth stage, weathering, and differ greatly in plant parts. Simplexin is found in all plant parts but is most concentrated in the seeds, and persists for extended period despite field weathering under extreme conditions.

In feeding trials *Pimelea* of known simplexin content was fed to young, previously unexposed steers in steadily increasing doses and their rumen and tissue levels of simplexin were followed for 120 days. Only minor poisoning signs were seen from 35 days onwards and levels of simplexin in their blood were almost undetectable. Poisoning signs diminished over time despite calves being fed increasing toxin doses. It was concluded that these calves, when exposed to prolonged low simplexin doses, developed mechanisms for detoxifying or metabolizing simplexin, presumably through rumen microbial adaptation, and this is consistent with observations that “experienced” cattle are better able to tolerate exposure to *Pimelea*. Our current research focuses on the development of a prophylactic oral drench or inoculum to degrade the toxin (before absorption), and hopefully prevent the incidence of poisoning.

Deconstructing molecular catalysis and self-assembly by advanced mass spectrometry and ion mobility; towards rationally designed molecular reaction vessels.

Nicole J. Rijs*

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Our understanding of molecular-level structure-function relationships has facilitated the rational design of compounds and materials for specific functions. For example, zeolites have highly engineered catalytic properties based on pore and active site structure,¹ while sophisticated supramolecular coordination cages have been recently developed as reaction vessels, promoting a range of encapsulated chemoselective, and even enantioselective reactions.² The key to effectively using these next generation vessels is an understanding of their structure reactivity relationships, and the sometimes unusual behaviours of the inner cavity, portholes and association properties. To date, these properties have been difficult to study both experimentally and theoretically.

In recent years, advances in instrumentation have led to tandem mass spectrometry/ion-mobility spectrometry of high enough resolution to be useful in measurement of molecular structure. This has led to these techniques being applied to a wide range of analytically relevant structural studies: from proteins assemblies and biomolecules such as carbohydrates, to polymers and materials compounds.

Herein, a combination of a novel ion-mobility apparatus and quantum mechanical computations was used to study, (i) isomer-resolved ion molecule reactions relevant to trifluoromethylation mediated by a copper oxide complex³ and (ii) structural and encapsulation studies of self-assembled cyclotricatechylene and cryptophanes,⁴ where ion-mobility and mass spectrometry have been key in deciphering the structure and reactivity. Ongoing research is aimed at studying the structure-reactivity relationships of host-guest assemblies with reactive properties, such as curcubiturils,⁵ and further development of techniques to investigate the intrinsic properties of capsule molecules that possess the potential to be reaction vessels.

Ring-Strain and Hypervalent Bonds: From Synthesis to Chemical Biology

Jérôme Waser

Laboratory of Catalysis and Organic Synthesis, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland
jerome.waser@epfl.ch

A fast access towards organic molecules of increasing complexity is one of the major motors of progress in multiple fields of fundamental and applied science, such as chemical biology, drug discovery or agrochemicals. To answer this need, our group develops new reactions based on the exceptional reactivity of hypervalent iodine reagents and strain rings, such as cyclopropanes and cyclobutanes.

Hypervalent Iodine Reagents:[1] The triple bond is one of the most versatile functional groups in organic chemistry, material sciences and chemical biology. Our group has introduced EthynylBenziiodoXolone (EBX) heterocyclic reagents for alkyne-transfer to X-H and C=C bonds as well as diazo compounds. This presentation will focus especially on the alkynylation of X-H bonds and applications in chemical biology.[2]

Aminocyclopropanes:[3] Activation of cyclopropanes with an amino and carbonyl groups led to exceptional reactivity in cyclization and annulation reactions. In particular, the development of selective formal homo-Nazarov reactions led to the efficient synthesis of the natural products goniomitine and jerantinine E, allowing the investigation of their bioactivity.[4]

References
Amino acid based anti-biofilm compounds

Jessica L. Harris

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The adhesion of bacteria to surfaces and their subsequent ability to form colonies called biofilms can cause significant health risks to humans and presents a major economic burden to society. Due to the fact that biofilms display extreme resistance to antibiotics, new approaches are needed to make surfaces unfavourable for bacterial attachment and proliferation. This thesis will explore a novel anti-biofilm approach that aims to incorporate the biofilm dispersal properties of nitroxides with antimicrobial peptides through the use of single amino acids coupled to a nitroxide.

The present work explores the synthesis and characterisation of new nitroxide-containing amino acid hybrid compounds and their methoxyamine derivatives. These hybrids utilise three Boc and/or Cbz protected amino acids (L-tryptophan, L-lysine and L-arginine) and three nitroxides (4-amino TEMPO, 4-amino TMIO and 4-amino TEIO) to form an amide bond between the free carboxylic acid moiety of the amino acid and the primary amine of the nitroxide. Subsequent deprotection of each hybrid produced the desired target compounds (shown in Figure 1) in excellent yields (92-95%).

Biological testing (to be conducted) will be used to determine whether these hybrids display any significant anti-biofilm activity, the results of which will inform the design of further hybrid compounds incorporating the anti-biofilm properties of both nitroxides and antimicrobial peptides.

Figure 1: Example target compounds: (a) Tryptophan-TEMPO, (b) Tryptophan-TEMPO (methoxyamine), (c) Lysine-TEMPO, (d) Lysine-TEMPO (methoxyamine), (e) Arginine-TEMPO and (f) Arginine-TEMPO (methoxyamine)
**Design, synthesis and biological evaluation of uridine-peptide conjugates as bisubstrate analogue inhibitors of human O-GlcNAc transferase (OGT)**

**Philip Ryan**\(^1\)\(^2\)\(^3\)\(^4\), **Andrew Davey**\(^1\)\(^2\)\(^3\), **Matt Alteen**\(^5\), **David Vocadlo**\(^5\)\(^6\), **Santosh Rudrawar**\(^1\)\(^2\)\(^3\)\(^4\)*

\(^1\) Menzies Health Institute Queensland, Griffith University, Gold Coast 4222, Australia
\(^2\) School of Pharmacy and Pharmacology, Griffith University, Gold Coast 4222, Australia
\(^3\) Quality Use of Medicines Network, Griffith University, Gold Coast 4222, Australia
\(^4\) School of Chemistry, The University of Sydney, Sydney, NSW, 2006, Australia
\(^5\) Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada
\(^6\) Department of Molecular Biology and Biochemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

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O-GlcNAc transferase (OGT) catalyses the post-translational addition of O-linked N-acetylglucosamine (GlcNAc) onto myriads of substrate proteins. This transfer takes numerous roles in biological processes, notably coupling metabolic status to regulation of varied cellular signalling pathways\(^1\)\(^2\). Inhibition of OGT has therefore become a desirable strategy to aid in understanding key biological processes and addressing pathological progression of chronic metabolic diseases such as cancer\(^3\). Moreover, inhibitors of OGT have potential to be developed into tools for cancer diagnosis.

Development of selective inhibitors of OGT has proven challenging with previous designs focussing on the high affinity earned by mimicking the universal donor uridine diphosphate (UDP). Additionally, as each transferase operates on numerous different protein substrates, peptide and peptidomimetics have so far been unable to supply the required potency to be of therapeutic value, though selectivity was improved. Recently the nature of ternary hOGT complexes have been observed and have facilitated the rational design of UDP-peptide bisubstrate inhibitors of OGT\(^4\). Here we discuss design and synthesis of a series of novel bisubstrate analogue\(^5\) conjugates [Fig. 1] as well as their inhibitory activity against hOGT.

**Figure 1.** General structure of novel bisubstrate OGT inhibitors


Organic and Medicinal Chemistry

Structure function relationships of a ribityl uracil antigen on T-cell activation

Geraldine Ler,1 Weijun Xu,1 Ligong Liu,1 Jeffrey Y. W. Mak,1 Alexandra J. Corbett,2 Xin Yi Lim,2 Andrew N. Keller,3 Wael Abdelhady,3 Jamie Rossjohn,3 James McCluskey,2 David P. Fairlie1

1 Australian Research Council Centre of Excellence in Advanced Molecular Imaging, Institute for Molecular Bioscience, The University of Queensland, Brisbane, Qld 4072, Australia
2 Department of Microbiology & Immunology, Peter Doherty Institute for Infection and Immunity, University of Melbourne, Parkville, Victoria 3010, Australia
3 Australian Research Council Centre of Excellence in Advanced Molecular Imaging, Department of Biochemistry and Molecular Biology, Monash University, Clayton, Victoria 3800, Australia
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A newly characterised class of T-lymphocytes known as mucosal associated invariant T (MAIT) cells was found to recognise a ribityl uracil derivative (5-OP-RU) which is a byproduct of the bacterial riboflavin biosynthetic pathway. In contrast to other classes of T-cells that recognise peptide and lipid based antigens, MAIT cells are the only class known to date to be activated by heteroaromatic molecules. MAIT cells are abundant in blood and mucosal tissues but their roles in human health and disease are still being elucidated. Ternary crystal structures of 5-OP-RU sandwiched between the MHC-like protein (MR1) and the MAIT T-cell receptor (TCR) show a hydrogen bonding network between the ribityl hydroxyls of 5-OP-RU, the TCR and MR1. We have synthesized a series of deoxygenated analogues of 5-OP-RU to dissect the contributions of ribityl hydroxyls to MAIT cell activation. A better understanding of these relationships is expected to aid in the design of future agonists and antagonists as probes for the MAIT TCR-MR1 axis. Herein we discuss some synthetic routes to these deoxygenated derivatives as well as early results from this study.

Figure. Hydrogen bonding interactions (dotted lines) between the ribityl tail of 5-OP-RU (black), MR1 (blue) and the MAIT TCR (red). Amino acids of proteins are abbreviated as one letter codes. α/β refer to the TCRα- or β-chain.
Synthesis of iminosugar uronidase inhibitors as potential pharmacological chaperones for MPS I and MPS VII.

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Mucopolysaccharidoses (MPS) are recessive genetic disorders characterised by a deficiency or lack of the enzymes required to degrade glycosaminoglycans, resulting in their accumulation within the lysosome. MPS I and MPS VII are caused by mutations to the enzymes α-L-iduronidase and β-D-glucuronidase, respectively. Starting with the cheap and readily available D-arabinose a divergent synthesis was developed to provide access to putative competitive inhibitors 1 and 2 to act as potential pharmacological chaperones for the aforementioned enzymes. The enantiomers of both targets are also readily targeted via the use of L-arabinose as the starting material.
Selective ARTD8 Inhibitors as a potential late stage prostate cancer treatment

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Prostate cancer is one of the leading causes of cancer-related mortality in Australia and around the world, due in part, to the inadequacy of current chemotherapeutics to overcome the androgen-independent nature of these late stage metastasises. Therefore, it is vital that new research targets the resistance of cancer cells, in order to improve patient prognoses.

The diphtheria toxin-like ADP-ribosyl transferase member 8 (ARTD8) belongs to a family of intracellular proteins which catalyse the post-translational addition of ADP-ribose moieties onto target proteins. It has recently been demonstrated that ARTD8 promotes the Warburg effect in hepatocellular carcinoma cells, and that ARTD8 levels are increased in cancer cells when compared to normal cells. In recently reported research when ARTD8 was blocked (using a shRNA knockdown model) the cancer cells had a significantly slower rate of growth while the normal cells growth rate was not affected.

Our research explores the structure, nature and function of ARTD8 using computational techniques and gives insight into the possibly targeting of ARTD8 over the other 18 ARTD enzymes.
Development of bicyclic nitroimidazoles as antitubercular and antiparasitic agents

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Infectious diseases are a major global health threat, causing significant mortality and morbidity every year. Despite the high incidence rate of these diseases, current treatment options are still inadequate and less efficient. Delamanid and pretomanid belong to the bicyclic nitroimidazole family that are currently in clinical development for treating drug-resistant tuberculosis. They also demonstrated repurposing potential against Leishmania donovani, parasites that are responsible to cause visceral leishmaniasis.1,2 Following the success of these nitroimidazoles, we have synthesized nitroimidazopyrazinones and nitroimidazopyrazines as two novel bicyclic series. These compounds displayed promising activity against a panel of parasite species (Giardia lamblia, Entamoeba histolytica and Trypanosoma brucei brucei) and Mycobacterium tuberculosis, with low toxicity against the mammalian cells. Most of the potent nitroimidazopyrazinones were stable in plasma and liver microsomes, while nitroimidazopyrazines showed interspecies variation in their metabolic stability. Similar to delamanid and pretomanid, some but not all of these potent analogues have limited aqueous solubility. Further modification was then conducted to optimise the solubility without affecting the potency. These findings give insight into the SAR of this scaffold and demonstrate its potential to be developed as anti-infective leads in the future.


A7 Organic and Medicinal Chemistry

Design, Synthesis and Biological Evaluation of Chemical Probes for Visualising DNA Synthesis in Proliferating Cells

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In the last decade ethynyl-2’-deoxyuridine (EdU) treatment followed by click chemistry to a fluorescent azide has become the mainstay chemical probe for labelling and detection of DNA synthesis in proliferating cells. However, EdU, as with other thymidine analogues, is reliant on nucleoside transporters (NTs) for cell uptake. Variation in expression of NTs within a cell population or between different cell lines raises the question of whether EdU is uniformly accessible for DNA synthesis and labelling with EdU comparable across different cell lines. Furthermore, EdU is cytotoxic and genotoxic in mammalian cell lines. To circumvent the drawbacks of EdU we proposed applying a pro-label approach. The pro-label approach is to chemical probes (or biolabels) as the prodrug approach is to drugs. We have recently applied the pro-label approach to EdU as proof-of-concept (figure 1).1 In this project we aim to develop a panel of new nucleoside derived chemical probes to visualise proliferating cells with improved pharmacological properties (uniform distribution, non-toxic) to EdU. These probes will allow long term labelling experiments across multiple proliferating cell types that is not possible with EdU. We plan to validate this approach in both two-dimensional (2D) and three-dimensional (3D) cancer cell culture to further understand the complex dynamics of tumour development and treatment.

Figure 1. EdU and ProEdU metabolic incorporation pathway into nuclear DNA

How reliable are the structural models used in drug design?

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The Protein Data Bank (PDB) contains more than 60,000 protein:ligand complexes. Structure–based drug design relies heavily on these structures and is critically dependent on their accuracy. Despite this, studies suggest up to 70% of ligands in the PDB were refined using inappropriate geometric restraints and in 25% of cases the binding interactions may be misleading (1). Current refinement and validation do not properly account for alternative protonation and tautomeric states, nor uncertainties in the stereochemistry, orientation and/or conformation of the ligand (2). Taking a series of high quality complexes of the aspartic protease Endothiapepsin (3), we have investigated whether it is possible to discriminate between alternative protonation states of the ligands and the active site aspartates using all-atom refinement incorporating electrostatic terms.

Light-activated nitrile-imine mediated reaction pathways for bioink synthesis in biofabrication

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Introducing cells to the additive manufacturing processes is becoming common in the emerging field of biofabrication. The materials used in the printing process are often cell-encapsulated hydrogels termed ‘bioinks’. Printing bioinks should involve relatively mild conditions in order to maintain a suitable environment for cell survival. This specification limits the reaction mechanisms available for gelation. One of the best ways to achieve spatiotemporal control during manufacturing is to use photo-activated reactions where the location, intensity and wavelength of light can be tuned to give specific properties. However, photochemically crosslinked materials currently require photoinitiator additives, which can be damaging to cells. Our research aims to utilise the previously developed nitrile-imine mediated tetrazole-ene cycloaddition (NITEC) and nitrile imine-carboxylic acid ligation (NICAL) reactions as photo-initiated reaction pathways for cytocompatible gelation, without the addition of any initiating agents. Natural and synthetic polymeric materials that are common to the bioprinting process such as gelatin or poly(ethylene glycol) have been functionalised with the proposed tetrazole moiety for the synthesis of bioinks.
Chiral induction through halogen bonding

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Halogen bonding is a non-covalent integration which has received considerable attention in recent years due to the strength and directionality of the interaction.\textsuperscript{1} Halogen bonds have been exploited for crystal engineering to create, among other things, networks that encapsulate cations. These networks are of interest due to the potential to control the spacing and arrangement of the cations allowing the properties of the crystals to be tuned.\textsuperscript{2} For example the optical and spin cross over properties of metal complexes can be manipulated by encapsulation in halogen bonded networks. Non-linear optical (NLO) properties are of particular interest to our group. Resolved metal complexes produce non-centrosymmetric crystals satisfying one of the requirements for second order NLO behaviour. This project investigates the potential to produce chiral crystals of metal complexes encapsulated in halogen bonded networks to create possibilities for the tuning/manipulation of the second order NLO. The metal complexes of interest include tris(1,10-phenanthroline)ruthenium(II) diiodide and the chloride, bromide and thiocyanate analogues which will be co-crystallised with halogen bond donors such as 1,2-, 1,3-, 1,4-diodotetrafluorobenzene and 1,3,5-triiodotrifluoro benzene. Also under investigation are the prospects for creating new methods for resolving chiral cations by encapsulation in chiral halogen boded networks. Progress has been achieved in both aspects of the project and will be presented in this seminar.

\textbf{Figure 1.} a) Halogen bonded network of Δ-tris(1,10-phenanthroline)ruthenium(II)) diiodide and 1,3,5-triiodotrifluoro benzene. b) Unit cell of tris(1,10-phenanthroline)ruthenium(II)) diiodide and (R)-2,3,5,6-tetrafluoro-4-iodo-N-(1-phenylethyl)benzamide

Identification and Quantification of dietary Anthocyanins and Metabolites in Human Urine

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Anthocyanins, the largest subclass of flavonoids, comprise a group of water-soluble phytochemicals known to be responsible for the deep rich red to blue-purple colours in fruits and vegetables. There is emerging evidence from epidemiological and experimental studies that suggests that a higher consumption of anthocyanin-rich foods is associated with a reduced risk for CVD¹. To better understand the potential mode of action of these dietary phytochemicals, their bioavailability and metabolic fate needs to be studied in more detail. Ten healthy male subjects were randomised to receive a single oral dose of 400mL anthocyanin-rich Queen Garnet plum juice (QGPJ) or 400mL water as a control, and, after a washout period of 2 weeks, the dosing and testing were repeated in a crossover fashion. Urine samples were collected quantitatively in two intervals up to 24 h after dosing (0-4 and 4-24 h). Urinary anthocyanins and metabolites were extracted using a solid-phase extraction (SPE) procedure and analysed by LC-MS (identification) and HPLC-PDA (quantification), respectively. The consumption of QGPJ resulted in the appearance of both native QGP/QGPJ anthocyanins (cyanidin-3-glucoside and cyanidin-3-rutinoside) and at least nine identified anthocyanin metabolites with intact flavlyium skeleton in the volunteers’ urine (0.18% of the ingested dose within 24 h). Cyanidin monoglucuronide, peonidin-3-glucosid, peonidin-3-rutinoside and peonidin monoglucuronide (peonidin is a methylated derivative of cyanidin) were the primary metabolites. Results from this study suggest that metabolites, and not the native QGP/QGPJ anthocyanins, are most likely the bioactive compounds in vivo. However, follow-up human trials using more anthocyanin-rich fruits/food are needed to identify the whole range of potential in vivo metabolites, especially the “low molecular” metabolites/degradation products generated by the colonic microbiota.

Queen Garnet plum (QGP) fruit

Main anthocyanins in QGP/QGPJ: cyanidin-3-glucoside (R1-OH, R2-OH, R3-glucose) and cyanidin-3-rutinoside (R1-OH, R2-OH, R3-rutinose)

Near-infrared fluorescent antibiotics for live cell and in vivo bacterial imaging

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Current standards in the diagnosis of bacterial infection lack the sensitivity and speed required to effectively treat serious infections. One modern approach to tackling this problem is in vivo diagnostic imaging, in which selectivity for the infection is achieved through attachment of components such as chemotactic peptides or antibodies to the imaging agent. Radioimaging technologies such as positron emission tomography (PET) and single-photon emission computed tomography (SPECT) have been used, but an emerging alternative is near-infrared (NIR) optical imaging, which is a more convenient, simple technique that can be used in real time. In this work, azide-alkyne click chemistry was used to attach a NIR-fluorophore to the antibiotic vancomycin, the use of which should give increased selectivity for bacterial infection. Live cell imaging of bacteria has been carried out showing successful labelling using the NIR-vancomycin probe. Application to in vivo imaging of bacterial infection should now be carried out to assess the viability of the probe for this exciting new area in diagnostic infection.
Design, synthesis and biological evaluation of C-5 substituted uridine analogues by using solid-phase microwave-assisted ligand-free Suzuki-Miyaura cross-coupling reaction

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Diverse pyrimidine nucleoside analogues substituted at the 5-position of the heterocycle and their corresponding 2’-deoxyuridine series have shown a variety of interesting biological activities resulting in numerous active drugs that are used clinically such as antiviral agents.\textsuperscript{1,2} In addition, the C-5-aryl/heteroaryl nucleoside analogues have been utilised as fluorescent probes for detection of genetic material in cells\textsuperscript{3}, as analytical tools in investigating RNA structure and function\textsuperscript{4}, as biosensor for detection of carbohydrate-active enzyme glycosyltransferases\textsuperscript{5}, and for the study of electron-transfer in an electrochemical DNA assay\textsuperscript{6}.

The binding motifs including sugar moiety (glycone) and nucleobase (aglycone) of these nucleoside derivatives are associated with a broad array of therapeutic importance in biological system. Among the nucleoside derivatives, introducing diversity into the aglycone moiety (base subunit, pyrimidine, uracil) represents promising strategies to improve binding affinity with target enzymes or to develop probes for sugar nucleoside utilising enzymes.\textsuperscript{7,8} For this perspective, a rapid access to a wide range of biologically active nucleosides a versatile approach to 5-substituted uridine analogues is required. This presentation discusses mild and practical reaction conditions for solid-phase Suzuki-Miyaura cross coupling of 5-iodouridine with various aryl/heteroaryl boronic acids, which can be extrapolated for the late stage modification of synthetically challenging uridine containing natural products, enzyme inhibitors or fluorescent biochemical probes.

![Figure 2: Synthesis of 5-aryluridines via Solid-phase Suzuki-Miyaura cross-coupling reaction](image)

Investigating the Relationship Between Phase Behaviour and Photovoltaic Performance

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Photocurrent generation in organic photovoltaic devices (OPV) can occur through two simultaneous charge generation pathways: photo-induced electron transfer from the donor to acceptor (Channel I) and photo-induced hole transfer from the acceptor to donor (Channel II). With recent interest in non-fullerene acceptor materials, there has been an increase in bulk heterojunction (BHJ) OPVs comprising materials which utilize both Channel I and Channel II pathways for charge generation. However, at present there is no simple way to determine the optimum donor/acceptor blend ratio or device architecture to maximize device performance.

Currently the most common method of evaluating new materials is to fabricate and test BHJ cells under a wide range of processing conditions to empirically determine the optimum blend ratio, with other measurements supporting the explanation. This is both a laborious and material intensive process. One of the most complex aspects of OPV devices is the film morphology, and methods to control it. Film morphology in BHJ solar cells can be controlled by the structure of materials in the processing solution, as well as post deposition treatments such as thermal annealing. For increased charge generation and extraction, the optimized BHJ film structure should ideally contain phases of pure donor and pure acceptor, along with intermixed regions of both materials.

A way to examine the microstructure of blended films is to utilize Differential Scanning Calorimetry (DSC) thermal analysis, and X-ray diffraction (XRD) techniques. By analysing films of varying donor/acceptor blend ratios with these methods, the relationship between film morphology and device performance can be explored. In this presentation we will discuss the recent development and understanding of predicting the ideal blend ratio within BHJ organic solar cells.
Wavelength Dependence of Light –Induced Cycloadditions

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The Planck-Einstein relation $E = h\nu = h\frac{c}{\lambda}$ describes the relation of frequency (wavelength) of light and photon energy. Consequently, control of irradiation wavelength and energy output as well as directionality of emitted light enables the use of photons as ‘reactants’ with a defined ‘stoichiometry’. We present methodologies for the precision photochemical study of light induced ligation protocols.1 Solutions of model compounds and the trapping agent N-ethylmaleimide are irradiated with monochromatic tunable laser light with a defined photon count at varied wavelength. The resulting conversion vs. wavelength plots (action plots) are powerful tools to derive quantum yields, support theoretical investigations into mechanistic details and provide guidance for the applications of the photoligation reactions.

![Figure 3](image)

Figure 3: Above: Mechanism of the photoligation of o-methylbenzaldehydes. Below: Relative energies (DFT calculations) of the transient species are shown for both the photochemical as well as a hypothetical thermal pathway (left). The singlet and triplet surfaces of the photoenol species (multireference calculations) are plotted in dependence of the dihedral angle of the hydroxy functionality, showing a conical intersection seam (middle). Experimentally determined quantum yields are plotted against wavelength (right).

Action plots for both the photoenolization of o-methylbenzaldehydes and the photolysis of diphenyltetrazoles (Nitrile Imine mediated Tetrazole Ene Cycladdition, NITEC) were obtained experimentally, employing nuclear magnetic resonance spectroscopy and high resolution electrospray ionization mass spectrometry. By a Beer-Lambert’s law assessment the action plots are rationalized and an iterative simulation of the photoreaction progress with spatiotemporal precision enables determination of quantum yields. Combination of the experimental results with density functional theory and multireference calculations allows insights into the mechanisms of the reactions involving conical intersections. The wavelength dependence of the photoactivation is discussed in the light of relative energies of the involved excited states. The results pave the way for precision photoreaction design and predictions as well as the development of orthogonal systems for advanced materials design.

Looking into the mirror: A detailed investigation into nudibranch mimicry

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Many animals closely resemble another species to protect themselves from predation. There are two main classes of mimicry: Batesian mimicry occurs when a palatable, undefended species (the mimic) mimics the appearance of an unpalatable, defended species. Müllerian mimicry exists when conspicuously coloured defended species evolve to resemble each other to increase their chances of survival against a common predator. Few studies have investigated such mimicry systems in the marine environment.

Nudibranchs from the order Opisthobranchia (Mollusca: Gastropoda) are slow moving, soft-bodied molluscs that appear to have limited physical defense against predation. Instead, they have evolved a complex strategy of protection that involve the employment of secondary metabolites to deter predators. Nudibranch taxa have evolved to sequester and utilise chemicals obtained from their diet. Many nudibranch species are described as aposematic, meaning they advertise their toxicity or unpalatability through highly conspicuous colourations and patterning. In this study, we investigated the nudibranch species Goniobranchus leopardus and Hypselodoris tryoni, which look very similar although they are not closely related. We investigated the chemical and spectral profiles, as well as, toxicity and palatability of Goniobranchus leopardus and Hypselodoris tryoni.
Naphthalene Flanked Diketopyrrolopyrrole (DPPN): A New Fused Aromatic Moiety for constructing high Performance Organic Semiconductors

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Diketopyrrolopyrrole (DPP) has been one of the most promising building blocks for constructing organic semiconducting materials used in organic field-effect transistors (OFET). As we have known, extended π-conjugated structure can facilitate intermolecular orbital coupling which determines the magnitude of the charge transfer integral and thus the charge transport in devices. What’s more, better intramolecular charge transport and intermolecular charge hopping depend on more superior morphology of the conjugated materials in thin film that is influenced by the flexible substitutions. Based on the above principles, it is worthy designing and synthesizing fused ring flanked DPP monomer with alkyl chains to exploit its potential use in OFET. In this work, we first synthesized and characterized a new diketopyrrolopyrrole (DPP) derivative, naphthalene flanked DPP with butyl-octyl side chain (BO-DPPN). When comparing with its thiophene- and furan-flanked DPP analogues using the same common alkyl chain, BO-DPPN shows most suitable nature for OFET application. For example, DSC analysis demonstrates its high degree of crystallinity, UV-Vis spectra show a strong aggregation in solid state, XRD pattern indicates its tight and long-range ordered lamellar packing. As expected, the OFET devices function well when using BO-DPPN directly as active semiconductor and an impressive hole mobility of 0.0126 cm²V⁻¹s⁻¹ was observed with a bottom-contact/top-gate architecture using solution processable approach indicating its promising potential for use in organic electronics. What’s more, the morphology of the conjugated materials in thin film where intramolecular charge transport and intermolecular charge hopping are happening can be optimized by appending suitable flexible side chains to the molecular backbone which will cause changes of several solid-state properties that include not only film morphology but also crystallinity and packing order. We further attached both linear (n-decyl and n-dodecyl) and branched (2-hexyldecyl) alkyl chains to our new DPP derivative. The thermal, photophysical properties, energy levels and molecular stacking orientation have been studied in detail. All the materials show thermal stability with a decomposition of up to near 400°C, high semi-crystallinity feature, moderate HOMO & LUMO energy levels, easily-forming excited states and different domain sizes in thin film. All the properties predict the potential use in organic thin film transistors. The bottom-contact/top-gate transistor devices based on n-decyl alkyl chain substituted monomer show the highest mobility of 0.019 cm²V⁻¹s⁻¹, with the Ion/Ioff ratio reaching 10⁶ order of magnitude. It is noted that naphthalene flanked DPP monomers were first synthesized in our group and unexpected high mobility in OFET devices were observed when using these monomers as semiconducting materials directly without any further chemical functionalization. Polymers and small molecules based on this new derivative are under way in our lab.
A reusable nanostructured substrate for the selective detection of Pb(II) ions

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Lead ion is an environmental toxicant known to pose adverse effects on humans and wildlife. Consequently, its early detection is vital for the development of control and remediation strategies. To achieve this, detection techniques that are sensitive and field deployable are required. Hence, a sensitive, selective and field deployable surface enhanced Raman spectroscopy (SERS) methodology was developed for the detection of Pb(II) ion in water using aminobenzo-18-crown-6 (AB18C6) and a reusable Au nanostructured substrate. Fluorescence spectroscopy was used to confirm the complex formation between AB18C6 and the target Pb(II) ions before SERS detection of the lead ions by a handheld Raman spectrometer. The detection methodology involved three steps: Pb(II)-AB18C6 complex formation, immobilisation of Pb(II)-AB18C6 complex unto a nanostructured substrate and Pb(II) ion detection from the loaded substrate by SERS. The substrate, bearing Pb(II)-AB18C6 complex, was cleaned by means of electrochemistry and reloaded for another Pb(II) detection cycle. The limit of quantification (LOQ) and limit of detection (LOD) for Pb(II) ions detection by the SERS method was 2.20 pM and 0.69 pM respectively. This LOD of 0.69 pM is five orders of magnitude lower than the maximum Pb(II) level of 72 nM allowed by the US Environmental Protection Agency in drinking water. This method has strong potential to detect other environmental toxicants by utilising the appropriate recognition molecule for a target analyte.
Can wastewater-based epidemiology be used for the assessment of anabolic steroid use?

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Anabolic-androgenic steroids (AAS) are exogenous substances, related to the male hormone testosterone. The muscle growth and strength enhancing properties of these compounds can lead to their misuse among athletes and are therefore prohibited by the World Anti-Doping Agency (WADA). Subsequently, checks are often performed on individual professional, in-competition athletes. For this reason the literature is generally focussed on the detection of AAS in biological matrices such as animal or human urine, hair, plasma or blood.

Wastewater-based epidemiology (WBE) is a concept that can be used to provide spatial and temporal information on the use of chemicals within a population without being invasive. Analytical methods such as liquid chromatography coupled to mass spectrometry can be used to detect and quantify chemicals such as licit and illicit drugs, personal care products and environmental contaminants in wastewater samples collected from the influent of wastewater treatment plants (WWTPs).

The aim of this project is to develop a robust, selective and sensitive method for the identification and quantification of multiple anabolic steroids in influent wastewater by using solid-phase extraction (SPE) with subsequent LC-MS/MS analysis. An LC-MS/MS and SPE method have been developed and optimised for these compounds. Following method validation and stability assessment, targeted analysis of influent wastewater from WWTPs in Australia will be performed. The improvement and validation of existing analytical techniques and the inclusion of a novel library of anabolic steroid compounds may be an approach to aid in understanding anabolic steroid use among defined populations when applied to WBE and would satisfy the requirement for further research in this area.
Active Metal Template Synthesis of a Switchable [2]Rotaxane in Solution and on the Surface

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A switchable [2]rotaxane is synthesised using the copper(I)-catalysed azide-alkyne cycloaddition reaction in an active metal template methodology. The [2]rotaxane exhibits switching dynamics based on an intramolecular coordinate bond between a pyridine-containing macrocycle and zinc metalloporphyrin axle. The solution system is then adapted to the TentaGel polystyrene resin bead surface which allowed the switchable dynamics of the surface tethered species to be characterised by 1H HR MAS NMR. The inclusion of zinc metalloporphyrins in the structure of the [2]rotaxane thread allowed the loading of surfaces to be assessed by LA-ICPMS in conjunction with elemental analysis.
Phytates and oxalates in Kakadu plum (*Terminalia ferdinandiana*): Toxins to be considered

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Global demand for food is increasing as well as the need to ensure sustainable and equitable food security. Composition of food is an area that requires exploration to ensure the safety of plant foods for human consumption. In this study, mineral, phytate and oxalate compositions were investigated to explore the nutritional and antinutritional composition of Kakadu plum (*Terminalia ferdinandiana*) tissues. Molar ratios and \textit{in vitro} mineral availability were also calculated to predict the implications for mineral bioavailability. The mineral concentrations in mg/100g on a dry weight basis (DW) of the fruits, leaves and seedcoats varied widely (sodium: 95-212, calcium: 131-1340, potassium: 264-2710, phosphorus: 20-73, zinc: 0.3-2.2 and iron: 1.7-3.9). Phytate content was highest in the leaves (6340 mg/100g) followed by fruits (3590 mg/100g) and seedcoats (1680 mg/100g) as DW. Fruits contain the highest level of oxalates (1420 mg/100g) compared to leaves (1130 mg/100g) and seedcoats (320 mg/100g) as DW. Phytate: calcium, oxalate: calcium, phytate: zinc and phytate: iron molar ratios were compared with the values that are commonly used for prediction of the \textit{in vitro} mineral availability and were found to be far above these critical values. The results revealed that Kakadu plum tissues contain considerable amounts of essential minerals like potassium, calcium, magnesium, iron and zinc but high contents of oxalate and phytate might cause decreased availability of these minerals. Therefore, detailed \textit{in vitro} bioaccessibility and absorption studies are necessary to predict the impact of these antinutritional compounds on the bioavailability of minerals in Kakadu plum as well as their potential toxicity for humans.
2D C3 Marfey’s Method for Amino Acid Analysis and Structure Elucidation in Peptidic Natural Products

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Structure elucidation and assigning the regiochemistry of enantiomeric amino acid residues in peptidic natural products has been a challenge, and often relies on either partial or total synthesis of multiple isomers. Here, we demonstrate application of the recently reported 2D C3 Marfey’s method for unambiguous positioning of L-Ala and D-Ala residues in Talarolide A, a novel cyclic heptapeptide hydroxamate, isolated from Australian marine tunicate-associated fungus Talaromyces sp. (CMB-TU011). Further, we set out to use the 2D C3 Marfey’s method as an analytical tool for structure elucidation of other linear peptides isolated from Talaromyces sp. (CMB-TU011) in small quantities. The 2D C3 Marfey’s method coupled with the high-resolution mass spectrometry (Q-TOF LC/MS) represents a valuable analytical technique for complete structure elucidation of minor peptidic natural products present in microbial extracts.
Something new in Hartree-Fock theory

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Hartree-Fock theory was first introduced in 1935, and has since become integral to modern quantum chemistry, in conjunction with density functional theory. More than 80 years later we provide a generalization of its core concepts to excited state ensemble systems[1], which can be used to calculate excitation spectra. Our approach is guaranteed to be unique, and to minimize the remaining correlation energy. Moreover, it naturally incorporates superposition physics. It thus points to new directions in quantum chemical understanding and simulation of excited states.

A Reaction Pathway Bifurcation in the (4+3)-Cycloaddition

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Evidence for the presence of a post-transition state pathway bifurcation in a model (4+3)-cycloaddition is presented. Density functional theory calculations (B3LYP/6-31G(d)) for the reaction of acrolein-BF$_3$ complex A and butadiene BD show that the gas-phase transition state structure TS-1 possesses significant (4+3)-character (in accord with previous investigations).$^{1,2}$ Intrinsic reaction coordinate calculations for TS-1 (which follow the minimum energy path) lead to the (4+2)-product. In contrast, when the reaction is modelled in implicit DCM, the solvent-phase transition state structure TS-1-DCM leads to the (4+3)-product. Relaxed potential energy surface scans demonstrate that the region after initial bond formation is relatively flat, with low energy paths to both (4+3)- and (4+2)-products through the same transition state. The results suggest that a large number of common (4+3)-cycloadditions are subject to “dynamic effects.”

Quantification of excipients in nutraceuticals using FTIR ATR and hand held Raman; preliminary results

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Legislation demands label on foods, medicines and nutritional supplements and that nutritional information displayed on these items be backed by reliable and validated analyses. Determination of complex nutraceuticals usually involves separation or isolation of the individual components before analysis with GC/HPLC. However, these procedures are lengthy and costly especially when involve many ingredients in a single formulation. We present an approach that is rapid, cost effective and also reliable for the determination of nutraceuticals using FTIR ATR or hand held Raman coupled with PCA-PLS techniques. Calibration models were built for each commercial formulation containing different excipients. The excipients were quantified and concentrations derived from the models correlated with the reference values on the labels. Recoveries within 84–116% were obtained. The method developed significantly reduces sample preparation time and cost of analysis.
SERS nanosensor for the clinical diagnosis of brain injury biomarker

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S 100 Beta (S100β) is a calcium-binding protein and used as a neuro-biochemical marker for brain injury and/or damage. It is also associated with neurodegenerative diseases like Alzheimer or other chronic neurological diseases. In this method, S100B was diagnosed in a biological sample using SERS nanosensor after complete rapid isolation from a complex plasma matrix using functionalized gold nanomaterials. These nanomaterials were prepared using magnetic gold nanoparticles decorated with selective S100B antibody fragments. The bare sites on the nanoparticles surface were occupied by alkanethiol layer to avoid non-specific binding from any other interfering proteins in the plasma. The functionalized nanomaterials were used for the rapid and selective isolation of S100B from plasma within 15 minutes. A magnet was used for the collection of S100B bearing nanomaterials from the plasma. The isolated protein was then released from the antibody capturing sites through the manipulation of the nanoparticles pH using a releasing buffer. The released protein was then purified, loaded onto a nanostructured gold substrate and detected by SERS with LOQ down to 100 pM. The method was cross validated against ELISA as the ELISA screening confirmed the presence of S100B in the released sample. The new method showed strong potential for the rapid and sensitive screening of other proteins biomarkers and environmental toxins in biomedical and environmental applications.
Pyrrolizidine Alkaloids – Natural Toxins Risk in Queensland Honey

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Pyrrolizidine alkaloids are widely distributed natural toxins and their consumption has been connected with acute and chronic liver damage, and even death, in wildlife, livestock and humans. There are more than 600 pyrrolizidine alkaloids, with the 1,2-unsaturated pyrrolizidine alkaloids being potent carcinogens. Their presence in food is concerning to food regulators, and Food Standards Australia New Zealand (FSANZ) have established a provisional tolerable daily intake for these alkaloids of 1 μg/kg BW/day.

Pyrrolizidine alkaloids occur in approximately 3% of flowering plants. Internationally it has been reported that such toxins can be found in honey due to transfer by bees of pollen/nectar from certain flowers, particularly Heliotropium, Crotalaria, Echium and Senecio species. Concern has been raised as to the extent of this contamination in Australian honey, but their presence in Queensland honey has not previously been examined.

Greater than 200 honey samples, sourced from markets and shops in Queensland, were analysed by UHPLC-MS/MS for 20 common pyrrolizidine alkaloids. Correlations between the occurrence of pyrrolizidine alkaloids and the botanical/geographical origin of the honey are essential as pyrrolizidine alkaloid contamination at up to 4000 μg/kg has been detected. In this study, the predominant alkaloids detected were isomers lycopsamine, indicine and intermedine, displaying identical MS/MS spectra. Separation of these isomers by UHPLC has enabled comparisons of the relative amounts present in honey to those amounts in east coast pyrrolizidine alkaloid containing plants. Notably, only low levels of alkaloids from Echium plantagineum (Paterson’s curse) and Senecio species were detected in honey. Plant pyrrolizidine alkaloid profiles will be compared to those found in honey samples.
Dynamic covalent chemistry at the solution:surface interface

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In the field of interlocked architectures, the development of industrial and medical applications, often require the attachment of the structures onto surfaces. However, the effect the surface has on the dynamic behaviour of the interlocked structures when attached to rigid surfaces is largely unknown. Furthermore, the characterisation of the surface bound supramolecular assembly is limited in their comparability to solution characterisation techniques, particularly in the absence of a redox or photo active group. This limitation can be overcome by the use of polymer resins as the solid support which allows the use of $^1$H High Resolution Magic Angle Spinning (HR-MAS) NMR technique for the analysis.

Traditional methods for the surface attachment of interlocked architectures is often limited by the irreversibility of the bond forming reaction which leads to undesired kinetic by-products, uninterlocked molecules, which contaminate the surface. In solution, dynamic covalent chemistry (DCC) has been shown to be successful in yielding complex interlocked architectures. This approach introduces a “proof-reading” mechanism into the system which ultimately leads to the formation of more of the thermodynamically favoured interlocked architecture. By combining the knowledge of DCC for the formation of interlocked architectures in solution we hope to improve the attachment of the interlocked assemblies onto polymer bead surfaces and determine their properties.

Chemical study of \(N\)-amino-\(L\)-proline methyl ester Schiff bases isolated from Fish-Gut derived fungus *Beauveria* sp.

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Chemical analysis of a *Beauveria* sp. (CMB-F563) led to isolation of a unique family of hydrazinyl Schiff bases of \(N\)-amino-\(L\)-proline methyl ester (1), prolinimines B-D (3-5). Structure elucidation of 3-5 was achieved by a combination of spectroscopic and \(C_4\) Marfey’s analysis, as well as total synthesis. Curiously, careful chemical analysis of the crude cultivation extract failed to detect either 4 or 5, but did reveal evidence of an "unstable" putative precursor, prolinimine A (2). The structure elucidation of 2 was subsequently confirmed by total synthesis, and co-injection with the crude extract. Of note, under mild (handling) conditions 2 underwent ready conversion to 4-5. Efforts to understand prolinimine biosynthesis prompted developing an analytical method for detection of the water-soluble precursor (1) in the microbial cultures.
New flavonoids and saponins from *Gynostemma pentaphyllum* (Thunb.) Makino

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*Gynostemma pentaphyllum* (Thunb.) Makino has been the focus of extensive research over the past decade and this interest and popularity has led the Australian regulator, the Therapeutics Goods Administration (TGA), to call for compositional guidelines. There are no official monographs for this herb. The work undertaken and presented here encompasses composition of total flavonoids and saponins (the principal active constituents) in *G. pentaphyllum*. Two new flavonoids (1 & 8) and five new triterpenoidal saponins (14, 15, 19, 22 & 23), together with sixteen known compounds (2-7, 9-13, 16-18 & 20-21) were isolated from the methanol extract of the leaves of *G. pentaphyllum* and ethanol extract of Active-AMP (a heat treated commercial preparation of *G. pentaphyllum*). Their structures were elucidated on the basis of chemical and spectral methods, such as HSQC, HBMC, COSY, NOESY, 1D NMR and UPLC and HRMS. A cell permeability assay, using Caco-2 cell model, on the isolated compounds is currently under analysis which will indicate the potential bioavailability of these compounds which can provide a better insight into the bioactivities of saponins and flavonoids from *G. pentaphyllum*.

**Flavonoids**

<table>
<thead>
<tr>
<th>Flavonoids</th>
<th>R₁</th>
<th>R₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. kaempferol-3-O-α-rhamnopyranosyl</td>
<td>H</td>
<td>rhamnose-galactose</td>
</tr>
<tr>
<td>(1→2)-β-galactopyranoside</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. kaempferol-3-neohesperidoside</td>
<td>H</td>
<td>rhamnose-glucose</td>
</tr>
<tr>
<td>3. rutin</td>
<td>OH</td>
<td>rhamnose-glucose</td>
</tr>
<tr>
<td>4. isoquercitrin</td>
<td>OH</td>
<td>glucose</td>
</tr>
<tr>
<td>5. quercetin-3-O-α-rhamnopyranosyl-[1→2]-α-</td>
<td>OH</td>
<td>rhamnose-rhamnose-galactose</td>
</tr>
<tr>
<td>rhamnopyranosyl-[1→6]-β-glucopyranoside</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. kaempferol-3-O-dirhamnoglucoside</td>
<td>H</td>
<td>rhamnose-rhamnose-galactose</td>
</tr>
<tr>
<td>7. kaempferol-3-O-dirhamnoglucoside</td>
<td>H</td>
<td>rhamnose-rhamnose-galactose</td>
</tr>
<tr>
<td>8. quercetin-rhamnoglucoside</td>
<td>OH</td>
<td>rhamnose-galactose</td>
</tr>
<tr>
<td>9. quercetin-rhamnoglucoside</td>
<td>OH</td>
<td>rhamnose-glucose</td>
</tr>
<tr>
<td>10.isorhamnetin-rhamnogalactoside</td>
<td>OCH₃</td>
<td>rhamnose-galactose</td>
</tr>
<tr>
<td>11.isorhamnetin-rhamnogalactoside</td>
<td>OCH₃</td>
<td>rhamnose-galactose</td>
</tr>
</tbody>
</table>

**Saponins**

12. gypenoside LvI, R₁=glc-glc, R₂=glc-xylo
13. gypenoside XLI, R₁=glc-glc, R₂=glc
14. gypenoside LvI acetate, R₁=glc-acetylglc, R₂=glc-xylo
15. gypenoside XLI acetate, R₁=glc-acetylglc, R₂=glc
16. gypenoside L (2015), R₁=glc-glc, R₂=OH, R₃=H
17. gypenoside Li (2015), R₁=glc-glc, R₂=OH, R₃=H
18. xynoside B (2015), R₁=glc-glc, R₂=H, R₃=OH
19. xynoside B1 (2015), R₁=glc-glc, R₂=H, R₃=OH
20. damulin A₁, R₁=glc-glc, R₂=OH, R₃=H
21. damulin B₁, R₁=glc-glc, R₂=OH, R₃=H
22. damulin E₁, R₁=glc-glc, R₂=H, R₃=OH
23. damulin F₁, R₁=glc-glc, R₂=H, R₃=OH
Applications of Liquid Chromatography-Mass Spectrometry (LC-MS) to Natural Products Explorations of New Zealand Marine Invertebrates

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Liquid Chromatography-Mass Spectrometry (LC-MS) has wide application to many fields and is especially useful in natural products chemistry. The variant liquid chromatography tandem-mass spectrometry (LC-MS/MS) is particularly powerful in this regard. For example, LC-MS/MS was utilised in the elucidation of the structures of analogues of the tripeptides janolusimide A\(^1\) and B\(^2\) obtained from nudibranchs\(^1,3\) and bryozoans\(^2,3\). This presentation will outline some of the applications of LC-MS to our research in natural products chemistry, through this and other examples.

\[
\begin{align*}
\text{Janolusimide A: } & R = H \\
\text{Janolusimide B: } & R = \text{CH}_3
\end{align*}
\]

Determination of pigments of purple sweetcorn using LC-PDA-MS/MS

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Purple plant pigments (anthocyanins), found in a range of fruit and vegetables (e.g. strawberry, plum, red grape), have been shown to possess various potential health benefits such as antihypertensive and anti-inflammatory activities, as well as preventative activities in age-related cognitive decline and memory loss. Although yellow sweetcorn does not normally contain anthocyanins, the current trial investigated the anthocyanin profile of purple sweetcorn, recently developed from purple Peruvian maize.

In this study, the anthocyanin content and profiles of purple sweetcorn harvested at different stages of physiological maturity were determined using an optimised extraction procedure and ultra-high performance liquid chromatography–accurate mass spectrometry (UHPLC-MS).

A total of twelve anthocyanin compounds, namely cyanidin-3-glucoside, cyanidin-3-(6''-malonyl)glucoside, cyanidin-3-(3'',6''-dimalonyl)glucoside, cyanidin-3-(6''-disuccinyl) glucoside, cyanidin-3-(6''-succinyl)glucoside, peonidin-3-glucoside, peonidin-3-(6''-malonyl) glucoside, peonidin-3-(dimalonyl)glucoside, pelargonidin-3-glucoside, pelargonidin-3-(6''-malonyl)glucoside, pelargonidin-3-(dimalonyl)glucoside and pelargonidin-3-(malonylsuccinyl) glucoside were identified and quantified in the purple sweetcorn samples, ranging in physiological maturity from 20 to 66 days after pollination.

Total anthocyanin concentration increased with increasing physiological maturity and was only present in the pericarp layer of the kernel. Interestingly, as kernels matured, the coverage of purple pigment increased from a small spot at the stigma-end of the kernel, gradually spreading towards the base of the kernel, so that the kernel pericarp became almost completely purple.

These results are important in regards to the development of strategies to increase the natural anthocyanin content (and potential nutritional quality) of purple sweetcorn.

[This study was funded by Horticulture Innovation Australia Ltd., project code: HN 15001]
Assessing important polyphenols and organo-sulfur compounds in selected varieties of Australian grown onions using Orbitrap LC-ESI-MS analysis

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There is currently great interest in bioactive compounds or phytochemicals from onions due to their molecular functionality and pharmacological effects1. Onion is not only an important vegetable worldwide, but also the fourth largest vegetable crop in Australia2.

The present study aimed to assess and to compare the main phytochemicals, polyphenols and organo-sulfur compounds, in selected Australian grown onion varieties, which included white, brown and red onions. Edible parts of the onions were freeze dried and ground into powder before subjecting to extraction and further chemical analyses as shown in the figure below. Target compounds were identified by Q Exactive LC-MS/MS (Thermo), and quantified by UPLC-PDA (Waters).

Phenolic compounds detected included anthocyanins, non-anthocyanin flavonoids and phenolic acids. L-alliin, an alliin isomer and methiin were found as main sulphur-containing compounds present in the onion samples. The red onion cultivar was found to have the highest concentration ($p<0.05$) of flavonoids, whereas the brown onions were highest in phenolic acids. However, the red onions were “unique” in terms of their anthocyanin content. The significant lowest amount ($p<0.05$) of flavonoids and phenolic acids was found in the white onions.

Organo-sulfur compounds, mainly L-alliin, were found at a comparable level in the three onion cultivars ranging from 280 to 360 mg/100g dry matter. The brown onions had the highest concentration of organo-sulfur compounds, followed by the red cultivar, and the white onions. However, there was no significant difference ($p>0.05$) between the red and white onions.

The present study generated novel and important information about Australian grown onion cultivars, their phytochemical profiles and potential functionality. This is a promising basis for future studies on the development of functional ingredients from Australian grown onions.

Illustration of selected Australian grown onion varieties under study.

Spatial assessment of some legacy POPs in estuarine sediment

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There is a deficit of data in literature on the trends of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and hexabromocyclododecane (HBCD) in the Brisbane River. Due to reports of their potential impact on ecological health, these compounds were assessed in sediment samples along a 71 km stretch of the Brisbane River. GC-MS/MS (PBDE and PCB) and LC-MS/MS (HBCD) analysis of the samples indicate concentrations (ng/g dry wt.) in the ranges; 0.01 – 12 (∑8 PBDE), 0.09 – 19 (∑7 PCB) and 0.04 – 9.9 (∑HBCD). This represents the first data for HBCD levels in sediment in the study area. Notably, BDE-209 contributed about 90% of the ∑8 PBDE concentrations which may reflect the higher usage of commercial-decaBDE products. Generally, sediments collected from the midstream (urban) section showed higher pollutant mean concentrations compared to upstream (agricultural) and downstream (industrial). Further work is encouraged, particularly to monitor HBCDs and also BDE-209 which can potentially degrade to lower and more toxic congeners since their usage has not been completely banned. Apart from bridging the data deficit, this result is useful for global budgeting of pollutants as well as estimating potential exposure to aquatic organisms and humans.

Keywords: Brisbane River, BDE-209, HBCDs, PBDEs, PCBs, Sediment
C1 Inorganic and Polymer Chemistry

Assembly of a $\text{M}_4\text{L}_6$ Tetrahedron from a Multidentate Organic Ligand

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The design of metal-organic systems that form with predictable and predetermined geometries, properties and functions is an important goal in self-assembly. Metal-organic frameworks (MOFs) are a class of porous materials which consist of metal ions coordinatively linked to multidentate organic ligands. In addition to thermal and mechanical robustness, these coordination polymers typically boast high surface areas and large pore volumes useful for selective encapsulation of smaller guest molecules. As MOF formation is generally carried out in a “one-pot” synthesis, the predictability of the resulting MOF structure and its properties have always been serendipitous. Through the use of the hierarchical self-assembly design strategy, metal-organic frameworks are able to be constructed with an unprecedented amount of control and predictability. This design strategy allows for predictably designed, customisable and highly controlled cages to be used as building blocks.

Here we report the synthesis of a new multidentate organic ligand and resulting discrete $\text{M}_4\text{L}_6$ tetrahedron cage. In addition to the internal cavity, this tetrahedron possesses some interesting and distinctly different binding pockets which may lead to allosteric effects in guest ingress and egress. Additional inbuilt functionality of the ligand allows for post-synthetic modification and additional complexation of the cage which may lead to the formation of a hetero-metallic and hierarchically self-assembled MOF.
Emissive lanthanide Ln(III) complexes have been shown to be useful for molecular imaging, facilitating reliable non-invasive real-time monitoring of fundamental biological processes.\cite{bunzli2005} Compared to existing organic dyes, these complexes can facilitate earlier and more accurate diagnosis and treatment of diseases in vivo.\cite{bunzli2005} However, since $f-f$ transitions are Laporté forbidden, direct excitation of Ln(III) metal ions is inefficient and hence strongly absorbing organic chromophores are typically required to act as an antenna, sensitising emission from the Ln(III) cation. Taking advantage of time-gated luminescence measurements, scattered excitation and autofluorescence from biological media can also be spectrally and temporally discriminated from the luminescent probe, allowing background free imaging and more precise quantification of the tagged targets.\cite{bunzli2010}

The bidentate 8-hydroxyquinoline (8-HQ) ligand has been previously used to prepare emissive complexes with lanthanide cations.\cite{deacon2011} Herein, we have combined the 8-HQ subunit with an additional pyridyl N-donor group, in order to synthesise the tridentate anionic ligand, 2-(5-methylpyridyl)-8-hydroxyquinoline (HMPQ). This ligand has been complexed with a variety of Ln(III) cations, forming several different classes of products that can be readily controlled by the reaction conditions. Representative members for each class have been structurally characterised (Fig. 1) revealing variable ligand to lanthanide metal ion ratios. We have also investigated the photophysical properties for these materials, which demonstrate relatively high photoluminescence quantum yields in the Near-Infra Red (NIR) region, and report our preliminary results for the Yb(III), Er(III) and Nd(III) complexes.

**Figure 1.** X-ray structures of [Yb(MPQ)$_2$(acac)] (Monoclinic $C_{2h}$, $R_1 = 3.64\%$), [Yb(MPQ)$_3$] (Monoclinic, $P2_1/c$, $R_1 = 4.57\%$) and [NaYb(MPQ)$_4$] (Triclinic, $P\overline{1}$, $R_1 = 4.03\%$).

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The design of functional interfaces is critical for almost every application, as the majority of materials interface with their environment. In particular, interfaces decorated with (functional) macromolecules fulfil critical functions in a range of devices and applications, covering areas from medical implants, 3D cell scaffolds, opto-electronics, sensors to coatings. The functionality of the interface and its interactions with the environment are critically determined by the type of polymer and, critically, the density with which the strands are tethered to the surface. We herein provide a discussion on the limits of physical grafting densities by applying a simple model. More importantly, however, we examine the three most employed methods for experimentally estimating grafting densities, i.e. dry thickness measurements, gravimetric assessment and swelling experiments. Critically, we provide for each of these a clear explanation of the inherent assumptions and introduce on this basis a prediction of the resulting errors in the determined grafting densities in a rigorous physical fashion using error progression. We demonstrate that the literature reported grafting densities are beset with a considerable error, which – however – can be minimized by selecting the correct experimental assessment. Finally, we make recommendations on how grafting density determinations should ideally be carried out and provide a perspective into future methods for grafting density determination.

Inorganic and Polymer Chemistry

Investigation of the fluorescence efficiency of profluorescent nitroxide adducts via electrochemical processes

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The electronic and optical properties of the profluorescent nitroxide diphenylanthracene was investigated and contrasted with the parent fluorophore. Electronic characteristics such as redox potentials, reversibility and diffusion coefficients were determined experimentally by cyclic voltammetry. The oxidation of all nitroxides in the study was found to be a quasi-reversible process while the reduction of the nitroxides appears irreversible. Optical properties including absorbance spectra, emission spectra and fluorescence quantum yields were collected with the use of UV-visible spectroscopy and spectrofluorimetry. Quantum yields of fluorescence of diamagnetic redox adducts of all the profluorescent nitroxide were also obtained through an in-situ technique with the use of concurrent fluorescence spectroscopy and electrochemical experimentation. Fluorescence-time profiles obtained from in-situ studies reveal that while the main redox pathway for parent fluorophore leads to a degradation of the fluorophore and loss of fluorescent properties, for the profluorescent nitroxide it was found the first redox process was associated with the nitroxide. This property means that the expected fluorescence emission is returned to the fluorophore even under conditions that would normally be detrimental. The effects of oxygen were also addressed through in-situ studies and cyclic voltammogram experimentation. The electrochemical in-situ technique also proved itself to be a powerful alternative to chemical oxidations and reductions demonstrating the ability to fine tune the redox reaction with more control compared with more conventional chemical switching of these molecules.
Design and synthesis of new chiral metal organic frameworks

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Metal-organic frameworks (MOFs) are class of metallo-supramolecular material that has received significant attention due to potentially useful properties such as regularity, porosity, robustness and high surface-areas, as well as complexity arising from interpenetration[1]. These properties lead to a wide range of applications including catalysis, gas separation, purification and storage[2]. In addition, chiral MOFs have employed in enantioselective separations because they have well organised pores suitable for specific guest binding and pore sizes which can be tailored accurately[3]. In the present study a series of chiral metal organic frameworks were designed and synthesised from new two different ligands with various metals (figure 1). The chirality of the materials was controlled through the introduction of stereogenic centres into one of the organic components. The successful formation of the target materials was confirmed by X-ray crystallography. The crystal structures of the chiral MOFs have shown a large void space in these MOFs which accommodate a large number of solvent molecules. This void space would be used for host-guest binding and enantioselective separation which is our aim for further studies.

Figure 1. The crystal structure of one of the synthesised chiral MOFs (Solvents and hydrogen molecules were removed for clarity purpose).

To date, extensive research efforts have been devoted to the improvement of solution-processed bulk heterojunction organic solar cells (OSCs) due to their advantages such as low cost, light weight and mechanical flexibility. Concerning the choice of materials, the majority of the high performance OSC devices have been reported using a wide range of functional conjugated donor materials (either small molecules or polymers) with fullerene-based either PC61BM or PC71BM molecules as the acceptor, which is commonly used acceptors in the OSC community due to their good electron mobility, superior electron affinity and an appropriate low lowest unoccupied molecular orbital (LUMO) energy level. Despite of the enhancement of the efficiency, the fullerene derivatives have some limitations including the limited light absorption in the visible and NIR regions, high cost, difficulty to purify, and poor morphological stability. To address these difficulties, various non-fullerene acceptors have been explored in the past few years and the efficiency of OSCs began to increase rapidly since 2010. One of the most distinct advantages of using non-fullerene electron acceptor materials is the range of options available in selecting various aromatic building blocks, especially the n-type electron withdrawing conjugated moieties.

Herein, a series of novel electron deficient small molecular acceptors based on 1,8-naphthalimide (NAI) and 9-fluorenone (FN) with different branched alkyl chains are synthesized and characterized. These molecules are based on an acceptor–donor–acceptor–acceptor (A1–D–A2–D–A1) molecular design configuration with NAI as the endcapping acceptor (A1), FN as electron-withdrawing central (A2) group, and thiophene ring as a donor (D) unit. These materials are named as NAI-FN-NAI (BO) and NAI-FN-NAI (HD) where BO and HD represent butyloctyl and hexyldecyl alkyl groups, respectively. To further modify energy levels, we converted the weak electron withdrawing ketonic group attached to the FN moiety of NAI-FN-NAI (BO) to a stronger electron withdrawing cyano group to obtain the compound NAI-FCN-NAI (BO). The materials exhibited higher to medium band gaps, low LUMO energy levels, and highly thermally stable properties. Among all new materials, OSC devices based on NAI-FN-NAI (BO) as an acceptor exhibit the highest performance with an open circuit voltage (VOC) of 0.88 V, a short-circuit current density (JSC) of 9.1 mAcm⁻², a fill factor (FF) of 45%, and an overall power conversion efficiency (PCE) of 3.6%. This is the first report of 9-fluorenone based nonfullerene acceptor with poly(3-hexylthiophene) donor in the devices with such a promising performance.
Poly(2-oxazoline)-Drug Conjugate Hydrogels as Implantable Drug Delivery Systems

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First synthesized in the 1960s, Poly(2-oxazoline)s are a class of polymers that have only recently attracted attention because of their rich and versatile chemistry and potential biomedical applications\(^1\). One unique feature of the poly(2-oxazoline)s is the possibility of directly incorporating high amounts of functional side-chains during polymerization by using various monomers enabling, for instance, post-polymerization crosslinking strategies to create hydrogels\(^2\). Recently, poly(2-oxazoline)s have been used as polymer-drug conjugates as a soluble drug delivery systems\(^3\), yet their use as polymer-drug conjugate hydrogels remains, to date, unexplored despite clear benefits. Hence, we aim to copolymerize 2-methyl-oxazoline (to increase hydrophilicity) and 2-undecenyl-2-oxazoline (for alkene group incorporation) using methyl triflate as the initiator. Subsequent use of thiol-ene conjugation chemistry to incorporate a model drug and crosslink the polymer is expected to produce drug delivery systems with potential use as an implantable device for animals (e.g. cattle, sheep, companion animals\(^4\)) and ultimately humans. Such a device may reduce adverse side effects seen in current drug delivery approaches and increase efficacy and safety of therapeutic substances\(^5\).

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pH-sensitive polymersomes as carrier for light-triggered encapsulation studies

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Self-assemblies from amphiphilic copolymers in aqueous medium, show great potential as vehicles for drug delivery and in synthetic biology.¹

Polyfunctional block copolymers are applied as building blocks for the formation of vesicular polymersomes.²,³ ATRP is used for the synthesis of block copolymers with defined block lengths and great uniformity. The self-organization of these macromolecules should take place in a short time to bring up stable polymersomes of low dispersity in morphology and size.⁴

After their crosslinking by UV light, higher stability as well as a pH-triggered change of permeability are reached via swelling and shrinking.⁵,⁶ In order to control the shrinking-swelling behavior using light as an external stimulus, a photo-acid is employed. To study the pH-regulated loading and release of drugs in vitro, a fluorescence model substance is used in our investigations. For studying the responsive behavior of polymersomes and their encapsulation activity, a variety of analytical methods such as DLS, GPC and AF4 were perfomed. The application of AF4 in combination with static and dynamic light scattering delivers information about the sizes and conformational properties of the polymersomes.⁷

After post and in-situ encapsulation of the fluorescence marker, the purification of non-encapsulated marker by hollow fiber filtration (HFF) is examined and characterized by fluorescence spectroscopy.

Modulation of Spin-Crossover Behaviour of Metal Complexes Encapsulated in Halogen Bonded Networks

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The field of crystal engineering comprises of various disciplines of chemistry and underpins the ability to modify and fine tune the properties of a crystal. Depending on which supramolecular building blocks are used, the resulting topology and geometry within the crystal structure can be slightly altered or completely transformed. This in turn can result in a change or amplification of the specific electronic functionalities of the crystal, such as the optical, magnetic, redox, electrical conductivity, spin-crossover, catalytic and luminescent properties.[1] The concept of spin-crossover (SCO) has been a topic of interest in the field of crystal engineering for almost 90 years, where one of the fundamental concepts is the notion of “cooperativity”. Here, the change in spin state of one metal complex within a crystal is enough to influence its neighbour into also undergoing SCO.[2] The degree of cooperativity within a crystal can vary, and is evident from the different SCO behaviours observed, e.g. abrupt, gradual, hysteretic (Figure 1.), in steps, and incomplete.[3] Furthermore, there exists a way to modify the SCO behaviour of a metal complex. By fine tuning the distances between neighbouring metal complexes and their intermolecular interactions (i.e. π–stacking, coordination as well as hydrogen bonds) the resulting crystals have the potential to change SCO activity.[4] This project aims to investigate the effects and methods in which metal complexes of a bis-iron(III) Schiff base type can be incorporated into halogen bonding frameworks. The addition of these frameworks will result in an additional chemical pressure being placed on the metal complexes, ultimately allowing for them to pack much closer together than in crystals of the pure complex, further increasing the degree of cooperativity and spin state switching potential of the crystals.

Figure 1. a) The crystal structure of [Fe(qsal-I)_2]OTf. b) The abrupt and hysteretic spin transition observed by [Fe(qsal-I)_2]OTf, through the variation in temperature.[5]

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

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

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

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Thiosemicarbazide ligands, like dithiocarbazate ligands are renowned for their ability to stabilise high oxidation state transition metal complexes due to the balance of conjugation and charge delocalisation found in the N-S chelate ring. Substituents (R, R') placed on the ring allow the electron density to be altered providing greater electron donating or withdrawing effects, overall altering the stability of the metal. The chemistry of the ligands below with transition metals like copper and nickel has resulted in complexes not always in high oxidation states. However, the behaviour exhibited in the presence of oxygen provides some novel redox properties, in addition to their potential to act as therapeutic cancer agents.

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\text{X} = \text{Cu, Ni} \\
\text{R} = \text{Methyl, Ethyl, Allyl, Phenyl} \\
\text{R'} = \text{Methyl, Phenyl}
\]
The Influence of Metal-Metal Distance and the Mechanism of Energy Transfer in NIR Luminescent Bimetallic Lanthanide Ruthenium Terpyridine Complexes

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In addition to organic ligands, photoactive d-block transition metal complexes, such as Ru(bpy)$_3^{2+}$ derivatives, have also been exploited as light harvesting antenna to sensitize the Near Infra-Red (NIR) emission from Yb(III) and Nd(III) containing complexes.[1,2] We have recently shown that Ru(tpy)$_2^{2+}$ derivatives can also be effective in sensitising NIR luminescence from the Nd(III) and Yb(III) cations via energy transfer from the metalloligand 3MLCT state to the Ln(III) excited state.[3]

The energy transfer efficiency in such systems is significantly influenced by the distance between the energy donor and energy acceptor. For bimetallic systems bridged by an organic ligand, the metal-metal distance can be controlled via modification to the ditopic bridging ligand. Altering the bridging ligand via conjugated extensions, such as phenyl rings, has the potential to also alter the photophysical properties of the metalloligand, which can also be further influenced by the presence of the coordinated Ln(III) cation.

Figure 1. X-ray crystal structures of the Ru$^{2+}$ terpy metalloligands a) [(toltpy)Ru(btpy)]$^{2+}$ (P21/n, R1 = 7.88%); b) [(toltpy)Ru(pbtpy)]$^{2+}$ (C2/c, R1 = 4.87%) and [(toltpy)Ru(ph2btpy)]$^{2+}$ (P1, R1 = 5.01%). Anion, solvent and H atoms have been omitted for clarity.

Herein, we have synthesised and characterised a series of modified bisterpyridine Ru(II) metalloligands (Fig.1), allowing the coordination and photophysical interactions with several Ln(III) cations (Ln = Yb, Nd, Er and Lu) to be explored. Using a combination of steady state, time resolved and ultrafast transient absorption experiments, the efficiency and mechanism of the energy transfer leading to the observed NIR luminescence has been characterized.

Halogen Bonded Supramolecular Networks containing Nickel(II) and Copper(II) complexes

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Halogen bonding is an emerging tool for constructing supramolecular network due to the relative strength and directionality of the interaction, allowing the controlled formation supramolecular materials. Organic compounds with pyridine functional groups have been explored extensively as acceptors in organic halogen bonded networks. Recent research on these compounds has investigated the selective formation of halogen bonds in compounds with multiple halogen bond accepting sites. Perfluorinated diiodoaromatics are used often in these studies due to their rigidity and strength of halogen bond interactions formed due to polarisation of the iodine atoms by the strongly electronegative fluorine groups.

![Figure 1. Ni$_4$ bpenda and 1,2-DITFB arranged in a zig-zag X-bond motif](image)

We have synthesised a range of nickel and copper complexes with divergent, non-coordinated pyridyl functional groups to act as halogen-bond acceptor units. Then, these complexes were co-crystallised with X-bond donor molecules 1,2-DITFB, 1,3-DITFB, 1,4-DITFB and 1,3,5-TITFB (DITFB = diiodotetrafluorobenzene, TITFB = triiodotrifluorobenzene). Crystal structures of the compounds obtained were determined.

Electrocatalytic water oxidation at amorphous trimetallic oxides based on FeCoNiO<sub>x</sub>

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Recently there has been a noticeable shift towards developing amorphous bimetallic or trimetallic oxides for electrochemical water splitting. However, the fabrication of a homogeneous mixed metal oxide electrocatalyst suitable for water electrolysis is not a facile process. Here we introduce an electrochemical synthesis method that is rapid, simple and performed under ambient conditions. Using this approach it is possible to create a catalytically active FeCoNiO<sub>x</sub>H<sub>y</sub> amorphous material whose activity is dependent on the nature of the underlying support. The trimetallic oxide is significantly more active than any single or bimetallic oxide combination for the OER. This amorphous catalyst demonstrates not only excellent activity but also stability over extended time periods.
A Ligand Field Assessment of Ni(II) in ZnAl$_2$O$_4$ Spinel

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Ni-doped ZnAl$_2$O$_4$, a spinel, exhibits a feature-heavy single crystal absorption spectrum due to the impurity ion occupying both cation sites which have different site symmetries ($T_d$ and trigonally distorted-$O_h$). The d-d absorption bands of the two chromophores show considerable overlap which can be differentiated via magnetic circular dichroism (MCD), as $O_h$ Ni(II) displays temperature-dependent C-terms in contrast to the four-coordinate site. Detailed ligand field calculations were then able to be made using the Angular Overlap Model (AOM), however, this highlighted discrepancies between theory and experiment such as the much less than expected splitting of the $^3T_{1g}$ ($^3P$) state by the trigonal field. Altering the cation distribution via synthesised Ni-doped ZnAl$_2$O$_4$ powders uncovered the presence of two distinct Ni(II) six-coordinate sites – one as a single ion in the host lattice and another that is influenced by a neighbouring Ni(II) ion in tetrahedral coordination. This scenario adequately resolves the uncertainties associated with the single crystal absorption spectrum.
Novel and Dopant-free Anthanthrone Dye-Based Organic Hole Transporting Materials for Cost Efficient and Highly Performing Perovskite Solar Cells

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To date, perovskite solar cells (PSCs) have gained a big attention in the solar cell community on account of the power conversion efficiency (PCE) increased quickly to world record 22% after the first achieved PCE of 3.8% in 2009. Even though the perovskite devices based on poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) as hole transporting material (HTM) is found to achieve the highest PCE of 22.1% up to date, polymeric HTMs have some detriments regarding the reproducibility of their synthesis and purification. In contrast to polymers, small molecules possess various benefits, including better batch-to-batch reproducibility, ease of purification, high purity, and definite structure. Part of small molecular HTMs for PSCs, 2,2',7,7'-tetrakis(N,N'-di-methoxyphenylamino)-9,9'-spirbiuorene (Spiro-OMeTAD) has been employed intensively as standard HTM. In spite of the remarkable performance (20.8%), some main shortcomings of Spiro-OMeTAD, including high cost and multistep synthesis, can impede the progress of economical and large area flexible PSCs. To address this issue, several organic p-type organic semiconductors with appropriate highest occupied molecule orbital (HOMO) energy level, strong absorption, high hole mobility, and low synthesis cost have been made.

In this work, we report two new simple cost efficient solution processable small molecular HTMs, namely TPA-ANT-TPA and ACE-ANT-ACE, using triphenylamine (TPA) and acenaphthylene (ACE) as end-capping groups with an anthanthrone (ANT) dye as π-conjugated core. Both novel materials without additives were implemented in mesoporous perovskite devices. While ACE-ANT-ACE based devices give efficiency around 13.1%, TPA-ANT-TPA ones achieves an overall efficiency of 17.5%. Notably, TPA-ANT-TPA exhibits an impressive stability compared to Spiro-OMeTAD under identical aging condition. Additionally, TPA-ANT-TPA possesses the low synthetic cost of $67/g compared to that of Spiro-OMeTAD ($91/g). A comparative study is prepared and pointed out that our new compound, TPA-ANT-TPA, is taken into account as the promising candidate to replace the currently used and prohibitively expensive hole collecting materials for conventional mesoporous layouts and large-area applications of perovskite solar cells.
Identification and Quantification of Indospicine and its Metabolites in Camel Tissue using UHPLC-MS/MS

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Indospicine (L-2-amino-6-amidinohexanoic acid) is a natural toxin found in the leguminous Indigofera plant species. This non-proteinogenic amino acid accumulates in tissues of animals grazing these plants, and it is known to cause both primary and secondary hepatotoxicosis. Dogs are especially sensitive to indospicine and in past decades, canine fatalities have occurred in Australia from the consumption of indospicine-contaminated horse and camel meat, most notably the death of domestic dogs in Perth in 2009 after the consumption of camel meat. This incident raised food safety concerns and as a consequence, the in vivo accumulation, excretion and distribution of indospicine in camel tissues was investigated in a feeding experiment. Indospicine has also been shown to be metabolised by rumen fluid to the metabolites 2-aminopimelamic acid and 2-aminopimelic acid. This study investigated whether these metabolites also accumulate in camel tissues particularly plasma.

The diet of six young camels (2-4 years, weighing 270-390kg) was supplemented with Indigofera spicata (337ug indospicine/kg bodyweight/day) for 32 days at which time camels 1-3 were euthanized. Plasma samples were collected throughout the trial and monitored for another 100 days after cessation of the diet in camels 4-6. Indospicine and the metabolites 2-aminopimelamic acid and 2-aminopimelic acid were measured on a Shimadzu Nexera X2 UHPLC system coupled with a LCMS-8050 triple quadrupole mass spectrometer and a UHPLC-QExactive orbitrap mass spectrometer (Thermo).

Indospicine levels in the plasma samples increased rapidly, with 50% of the maximum level (1.97ppm) after 6 to 13 days of feeding. After cessation of the treatment levels slowly decreased reaching the 50% mark after approximately 1 month, with low levels still present 100 days after cessation of the feeding trial. The metabolite 2-aminopimelamic acid could be detected at low levels (<LOQ) in almost all plasma samples, whereas 2-aminopimelic acid could not be detected. This suggests a rapid degradation of the 2-aminopimelic acid. Neither of the metabolites appear to accumulate. The slow depletion of residual indospicine however demonstrates the potential for secondary food poisoning for other animals like dogs.

![Concentration-time-plots of Indospicine in Camel Plasma](image)

2Tan ETT et al., J Agric Food Chem, 65: 7528–7534