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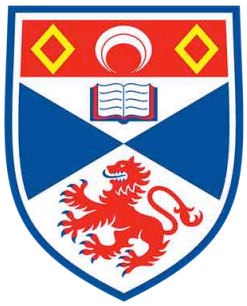

University of
St Andrews

EaStCHEM Conference for Early Career Researchers

#ECECR2017

Thursday 7th September 2017
University of St Andrews
(School of Physics and Astronomy)

The organisers would like to thanks all our generous sponsors, who made it possible to present ECECR2017

EaStCHEM Conference for Early-Career Researchers 2017
University of St Andrews
Thursday 7th September 2017

0930–1000 **Registration, Welcome Coffee and Poster Hanging**

1000–1110 Session 1 – Academic Keynote Address (Physics Theatre A)

1000–1010 Welcome and Opening Remarks
Prof. David O'Hagan

1010–1100 **KEYNOTE SPEAKER –** Dr Alyssa-Jennifer Avestro *(Durham University)*
Life in the Fast Lane: Catalysing an independent career & making it all count

1100–1110 **Comfort Break**

1110–1210	**Session 2 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Eoin Gould*	Physics Theatre C *Chair: David McKay*
1110–1125	Photoaffinity labelling identifies the target of trypanocidal bis-tetrahydropyran 1,4-triazoles **Lindsay B. Tulloch**	Pump-probe simulation of CS_2 and CHD: time-dependent photoionization **Maria Tudorovskaya**
1125–1140	Serine palmitoyltransferase protein interaction landscape and structural characterisation **Van Kelly**	Ador synthesis realized by use of the hydrostatic pressure **Michal Mazur**
1140–1155	Imaging intracellular drug distribution using stimulated raman scattering microscopy **William J. Tipping**	Manipulation of polar order in ferroelectric 'Empty' tetragonal tungsten bronzes **Jonathan Gardner**
1155–1210	Ensemble based drug design: a new paradigm in drug discovery **Jordi Juárez-Jiménez**	Synthesis of magnetic polyhedral: cubes and triangular bipyramids **Sergio Sanz**

1210–1340 Lunch, Exhibition and Poster Session (School of Physics Common Space)

1340–1440	**Session 3 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Tamara Kosikova*	Physics Theatre C *Chair: Amanda Jarvis*
1340–1355	Mechanistic studies on nucleophilic trifluoromethylation of carbonyls with the Ruppert-Prakash reagent **Thomas West**	Structure and reactivity of Cu-doped Au(111) surfaces **Federico Grillo**
1355–1410	Aryloxide-facilitated catalyst turnover in α,β-unstaurated acyl ammonium catalysis **Mark D. Greenhalgh**	Development of peptide-based electrochemical sensors **Eva González-Fernández**
1410–1425	Studying the mechanism of C–O cleavage in lignin model compounds by ruthenium-xantphos catalysis **Rebecca C. How**	*In-situ* thermal battery discharge using NiS_2 as a cathode material **Julia Payne**
1425–1440	Towards the rational design of isoform-selective cyclophilin ligands **Alessio De Simone**	Whither crystallography… A view from the ground **David B. Cordes**

1440–1510 **Afternoon Coffee** (School of Physics Common Space)

1510–1540	**Session 4 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Mark Greenhalgh*	Physics Theatre C *Chair: Rebecca How*
1510–1525	Single-molecule transmembrane supramolecular chemistry **Stefan Borsley**	Molecular magnets under pressure **Helen Duncan**
1525–1540	Capsules for molecular recognition and catalysis **Vicente Marti-Centelles**	Difference in reactivity of two zinc binding plant metallothioneins isoforms **Hasan Tanvir Imam**

1540–1550 **Comfort Break**

1550–1650 **Session 5 – Industry Keynote Address** (Physics Theatre A)

1550–1640 **KEYNOTE SPEAKER –** Dr Nathaniel Cain *(Afton Chemical)*
An Engineer's Career Path to Chemistry and Exploiting the Interface

1640–1650 **Concluding Remarks and Prizegiving** (Physics Theatre A)
Neil Keddie and Amanda Jarvis

1650–1800 **Wine Reception** (School of Physics Common Space)

[END]

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The Edinburgh and St Andrews Research School of Chemistry

EaStCHEM Conference for Early-Career Researchers 2017

Keynote Abstracts

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EaStCHEM Conference for Early-Career Researchers 2017

LIFE IN THE FAST LANE: CATALYSING AN INDEPENDENT CAREER & MAKING IT ALL COUNT

Author: Dr Alyssa-Jennifer Avestro

Affiliation: Durham University, Department of Chemistry

e-mail: alyssa.j.avestro@durham.ac.uk | @*ajavestro*

Author's Biography

Dr Alyssa-Jennifer Avestro received her BS degree (2006-10) from the University of California at Berkeley, where she trained in polymer nanoparticle synthesis and catalysis with Prof Jean Fréchet. Following a brief summer position at NanOasis Technologies, she completed her PhD at Northwestern University (2010-15) under the supervision of 2016 Nobel Laureate Sir Fraser Stoddart *FRS*. Her thesis focused on the manipulation of 1D and 3D electron delocalisation in organic materials utilising novel MIM scaffolds and shape-persistent macrocyclic geometries. Currently, Alyssa holds a three-year Royal Commission 1851 Research Fellowship at Durham University, which has enabled her to establish her early-career independence and research programme targetting the rational design of macromolecular and hierarchically-assembled optoelectronic organic materials.

Current Research Interest

Chemistry: *this* is the 'central science.' Never has the pursuit of it been more intellectually exciting or critically relevant to our society as it is today. We are privileged to practise our craft in the 'Golden Age' of chemistry, where fundamental intentions are more frequently leading to serendipitous discovery of new applications and real-world relevance—provided we are observant to see and keen enough to pursue them! Ironically, however, our ability maintain security and positive trajectory on the academic career path has never been more challenging as it is today as well. Here, I provide the unvarnished truths of my own experience (still) navigating my climb through the academe: How did a freshly minted PhD student convince a foreign Fellowships panel to give her a shot at independence? How do I keep a young research group funded and afloat despite the inherent challenges of being '*too* early career,' 'not a UK national,' 'a fixed-term employee,' 'a woman in STEM?' How has networking, demonstrating my value to others, and even the whirlpool of social media influenced my career trajectory? Are professional development programmes in communication, leadership, and innovation (e.g., *SciFinder Future Leaders*) really worth the time? Do I have a life outside of work? And what was it *really* like to work with a Nobel Laureate and experience Stockholm?

Spotting unlikely opportunity, then having courage to pursue it, has not only been a recurring theme in my scientific research*[1,2], but has also played a huge role in developing my career as it stands today. From interpreting my personal experiences of life in the fast lane, it is my hope that early career chemists can glean some perspective on the difficulties and utter joys of the academe that lie ahead, learn to make the most of their time—our most precious currency—and become their own catalyst[3] towards achieving academic excellence.

*Come learn about my love affair with naphthalene diimides (NDI), a rather traditional electroactive π-system, and how forays[1,2] into rationally designing their through-space interactions—along with other functional π-motifs—throughout the course of my training have influenced my own independent research goals in structure–property evaluation, optoelectronic materials development and energy storage.

References:

1. A.-J. Avestro, et al. *Angew. Chem. Int. Ed.* **2014,** *53*, 4442–4449.
2. D. Chen†, A.-J. Avestro†, et al. *Adv. Mater.* **2015**, *27*, 2907–2912.
3. A.-J. Avestro, *Chem* **2016**, *1*, 13–15.

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An Engineer's Career Path to Chemistry and Exploiting the Interface

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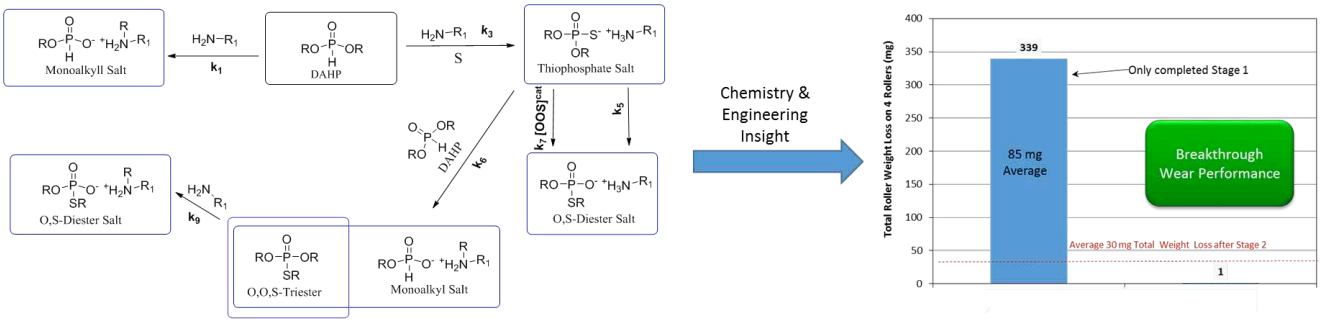
Affiliation: Afton Chemical Corporation

e-mail: Nathaniel.Cain@AftonChemical.com

The beginning of my scientific career started in Mechanical and Chemical Engineering, while working in the lab for professors ranging from organic chemists to thermodynamicists. During that time I helped start an undergraduate consulting company, where I was the VP and Technical Director. I later went on to graduate school in Chemical Engineering then went back to a small R&D and Consulting Company. In 2011 I joined Afton Chemical Corporation where I work as a Sr. R&D Engineering Specialist in Applied Research for Engine Oil Development. Much of my career has focused on the interface between chemistry and engineering.

The development of new products often initiate from different starting points. In many cases, new products are developed to fix an inherent weakness, usually a secondary performance attribute or no harms criteria, exposed in an existing product. An alternative, rarer opportunity, stems from an unmet primary performance need and results in a completely new space for product development. Whichever path a product takes, the development quickly becomes a multidisciplinary development effort. Exploiting the interface between chemistry and engineering is commonplace during scale-up. Leveraging this practice earlier in the research process for identification of performance chemistries is less often leveraged, but offers an opportunity to develop unique solutions.

The development of a Monothiophosphate Ester product will be discussed to demonstrate how the interface between chemistry and engineering led to a unique approach to Product Development. Monothiophosphate Esters are critical to the performance of lubricants for their antiwear characteristics. Control of the byproduct formation during synthesis is critical to the overall performance. Developing the full reaction network required a multidisciplinary effort, which ultimately led to a more robust product and process. Moreover, the work resulted in subsequent spin-offs that have resulted in a better understanding of our products performance chemistry and a subsequent product with breakthrough wear performance.



Oral Abstracts

Stream A Talks

Physics Theatre A

EaStCHEM Conference for Early-Career Researchers 2017

PHOTOAFFINITY LABELLING IDENTIFIES THE TARGET OF TRYPANOCIDAL BIS-TETRAHYDROPYRAN 1,4-TRIAZOLES

Author: Lindsay B Tulloch
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Author's Biography

Lindsay obtained his PhD in Structural Biology and Biochemistry at the University of Edinburgh, where his research focused on the structure-based design of anti-parasitic drugs. He continued this research at the University of Dundee, where he also investigated antibody-based antiviral therapy development and mechanisms of cell regulation. He now works at the University of St Andrews investigating drug-target interactions in parasites.

Current Research Interest

Over 65 million people in sub-Saharan Africa are at risk of developing African sleeping sickness [1], a usually fatal disease caused by infection with the insect-spread protozoan parasite *Trypanosoma brucei*. Current drug treatments are inadequate and new therapies are urgently required. Previously [2] we reported the synthesis and promising trypanocidal activity of compound 1, a bis-tetrahydropyran 1,4-triazole developed through a phenotypic screening assay. This study aims to identify the protein target(s) of compound 1 in *T. brucei* and understand its mode of action to aid further inhibitor structural optimisation.

To identify targets, compound 1 was functionalized with UV-reactive diazirine and "click"-compatible alkyne substituents to generate a bi-functional photo-affinity analogue, compound 3, which retained trypanocidal activity. Bi-functional compound 3 was UV cross-linked to its target in procyclic *T. brucei* in vivo and biotin affinity or Cy5.5 fluorescent reporter tags were subsequently appended by Cu(II)-catalysed azide-alkyne cycloaddition. The biotinylated protein adducts were enriched/isolated with streptavidin affinity beads and subsequent LC-MSMS identified the FoF1-ATP synthase (mitochondrial complex V) as a potential target.

Mitochondrial complex V was confirmed to be the target via a number of biochemical assays. We show that (i) compound 1 decreases cellular ATP levels (ii) by inhibiting oxidative phosphorylation (iii) at the FoF1-ATP synthase and (iv) that our compounds interact specifically with both the α- and β-subunits of the complex. Modeling indicates that they bind within the nucleotide-binding sites at the interfaces between the α- and β-subunits. The FoF1-ATP synthase is essential to *T. brucei* and its identification as our target now allows us to further optimise inhibitor potency and selectivity along the drug discovery pipeline. Furthermore, the photoaffinity labeling methodology employed here can be readily applied to other drug discovery programs to identify targets of drugs with unknown mode of action.

References:
1. P. G. Kennedy, *Lancet Neurol.* **2013,** 12, 186-194
2. G. J. Florence, A. L. Fraser, E. R Gould *et al*, *Chem. Med. Chem.* **2014,** 9, 2548-2556

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SERINE PALMITOYLTRANSFERASE PROTEIN INTERACTION LANDSCAPE AND STRUCTURAL CHARACTERISATION

Author: Dr. Van Kelly

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Author's Biography

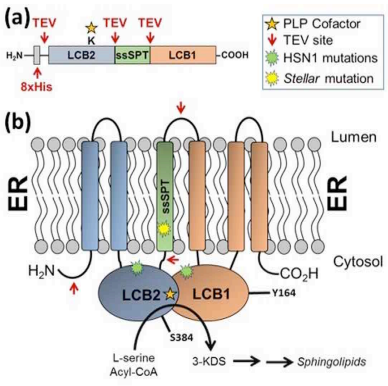
I studied biological sciences and computer science at the University of Auckland, New Zealand. My career in mass spectrometry started with high throughput nutraceutical screening for the New Zealand dairy industry. Upon moving to Scotland to undertake a PhD, my focus shifted towards cellular proteomics and the ubiquitin system. In my current position at Edinburgh University School of Chemistry, I use mass spectrometry to probe the structure and function of enzymes, including enzymes perturbed in human disease and enzymes engineered to synthesise novel substrates.

Current Research Interest

Background: Serine palmitoyltransferase (SPT) catalyses the first step in de novo sphingolipid biosynthesis. SPT condenses L-serine and palmitoyl-CoA to produce 3-ketodihydrosphingosine (KDS), a precursor to sphingosine, ceramides, sphingomyelin, and glycosphingolipids [1]. The human enzyme is a complex of three proteins (LCB1, LCB2, and ssSPT) and is endoplasmic reticulum (ER) membrane bound [2]. Mutations in SPT cause human sensory neuropathy type 1 (HSAN1) resulting in progressive neuronal degradation. SPT mutants have been shown to synthesise toxic deoxy-sphingolipids from alanine and glycine rather than serine [3], although the exact pathological mechanism is not known. Regulation of SPT is not well understood and the protein interaction landscape has not been fully characterised.

Methods: BirA(R118G)-SPT gene fusions were used for biotin proximity labelling to isolate interacting proteins from both human and yeast cells. The human SPT complex was also expressed and purified from the yeast ER as a single gene fusion. Purified protein has enabled kinetic studies as well as structural analysis using lysine reactive crosslinking reagents.

Results: Known and novel putative SPT interactors have been identified through biotin proximity labelling. A gene ontology analysis of interactors highlighted membrane organisation and ER-golgi transport. Activity assays confirm that purification of the fusion-enzyme in n-dodecyl-beta-maltoside micelles yields active protein. Lysine-lysine crosslinking and mass spectrometry analysis gives support to a structure modelled on the bacterial SPT homodimer.



Conclusions: Putative protein interactors suggest SPT may play an important role in membrane organisation and transport, or alternatively, SPT regulation may be mediated by enzyme localisation. Independent analyses are underway to validate putative SPT interactors. Additionally, in the absence of a crystal structure, crosslinking has provided a crucial insight into the structure of the SPT complex.

References:

1. A. H. Merrill. Chem. Rev., 2011, **111**, 6387-6422.
2. K. Gable, H. Slife, D. Bacikiva, E. Monaghan, T. M. Dunn, J. Biol. Chem., 2000, **275**, 7597-7603.
3. A. Penno, M.M. Reilly, H. Houlden, M. Laurá, K. Rentsch, V. Niederkofler, E. T. Stoeckli, G. Nicholson, F. Eichler, R. H. Brown, Jr., A. von Eckardstein, T. Hornemann. J. Biol. Chem., 2010, **285**, 11178-87

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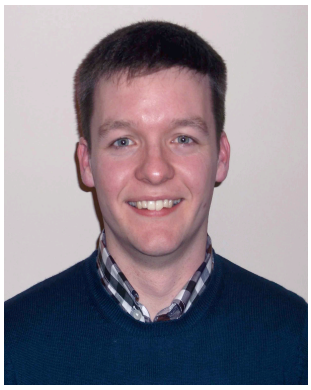
Imaging intracellular drug distribution using stimulated Raman scattering microscopy



Author: William J. Tipping

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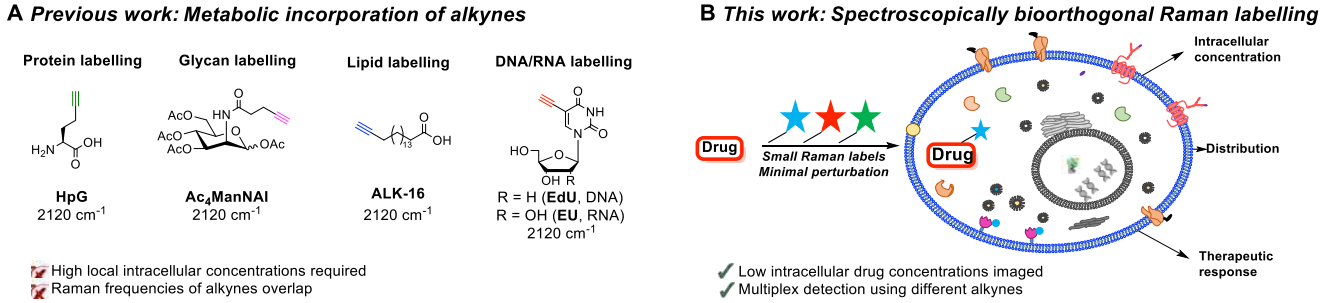
Author's Biography

William received his MSci. in Chemistry from the University of Nottingham in 2013 before completing a PhD in Raman imaging at the University of Edinburgh in 2017 with Prof. Alison Hulme and Prof. Valerie Brunton. He is currently a BBSRC-funded postdoc in the group of Prof. Alison Hulme at the University of Edinburgh, where he is using Raman imaging techniques to profile intracellular catalysis of bioorthogonal conjugation reactions.

Current Research Interest

Rapid advances in the field of Raman imaging, particularly stimulated Raman scattering (SRS) microscopy are opening up many new avenues for imaging and quantification of drugs and small molecules in living systems.[1] As a result, images of small molecules within cells might be acquired without the use of "bulky" fluorescent labels, (which may be as big as the small molecule under observation) or the use of nanoparticle sensors (which might perturb cellular biology). Previously, metabolic incorporation of alkyne-containing precursors has enabled direct intracellular visualisation of a range of cellular components using SRS microscopy (**Figure 1A**).[2] However, the detection of compounds with low intracellular concentrations remains challenging and in these instances, a Raman labelling approach may facilitate detection. Spectroscopically bioorthogonal Raman labels, including alkynes and nitriles, produce spectrally isolated peaks in the bioorthogonal region of the Raman spectrum (1800 – 2800 cm^{-1}) and can be used for direct intracellular visualisation by SRS microscopy.[2] Here, a series of Raman-active labels has been designed and evaluated for drug labelling studies (**Figure 1B**).[3] Real-time SRS imaging of drug uptake is then demonstrated using a multi-modal imaging approach to identify novel aspects of drug activity *in vitro*.



References:

1. **W. J. Tipping**, M. Lee, A. Serrels, V. G. Brunton and A. N. Hulme, *Chem. Soc. Rev.* **2016**, 45, 2075–2089.
2. L. Wei, F. Hu, Y. Shen, Z. Chen, Y. Yu, C.-C. Lin, M. C. Wang and W. Min, *Nat. Methods* **2014**, 11, 410–412.
3. **W. J. Tipping**, M. Lee, A. Serrels, V. G. Brunton and A. N. Hulme, *Chem. Sci.* **2017**, *advance article*.

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Ensemble Based Drug Design: A new paradigm in drug discovery

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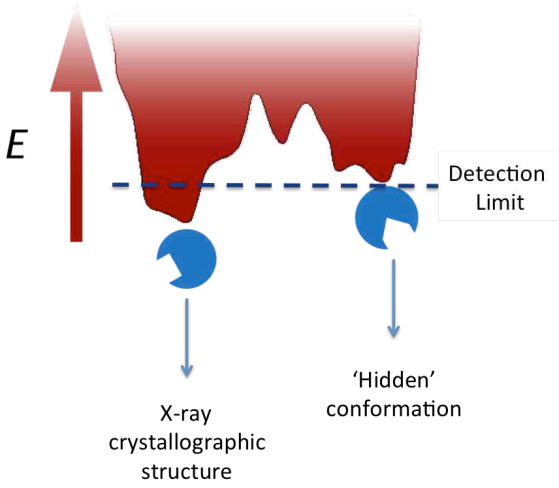
Author's Biography

I am a Marie Sklodowska-Curie Fellow with Dr Julien Michel at the EaStChem School of Chemistry of the University of Edinburgh, United Kingdom. I received my B.S (Pharmacy, 2009), M Sc and PhD (Biomedicine, 2014) from the University of Barcelona and during 2015 I was a postdoctoral fellow with Prof. Adrian Roitberg (University of Florida). I am interested in molecular recognition with main focus on rational drug design, especially for the selective inhibition of the Cyclophilins family.

Current Research Interest

X-ray structures have being highly influential in many drug discovery efforts over the last three decades. They constitute an invaluable tool for the characterization of the binding mode of small molecules and allow the rationalization of Structure-Activity Relationships (SAR). Nevertheless, since X-ray crystallography provides little information about the dynamic behavior of a protein, they constitute only a partial description. The Ensemble Based Drug Design (EBDD) approach intends to move away from this static view of proteins towards leveraging protein ensembles to rationally design small molecules able to modulate protein function.

On this talk I will present an overview of the molecular simulations approaches and analysis algorithms that Michel lab is developing to provide proof of concept for EBDD. I will focus on how molecular simulations and biomolecular NMR can be combined to unlock new opportunities for the discovery of Cyclophilin A inhibitors.



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Mechanistic Studies on Nucleophilic Trifluoromethylation of Carbonyls with the Ruppert-Prakash Reagent

Author: Thomas West
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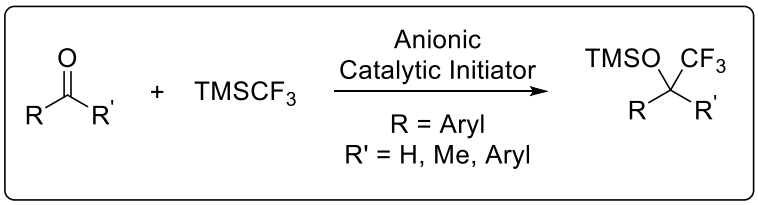
Author's Biography

Tom completed his MSci degree at the University of Bristol in 2012, where he worked with Prof. Varinder K. Aggarwal FRS on the synthesis and use of sulfonium ylides. He subsequently moved up to Scotland to conduct his PhD studies under the supervision of Prof. Andrew D. Smith at the University of St Andrews, working on catalytic enantioselective [2,3]-rearrangements of allylic ammonium ylides. In late 2016 he moved down to Edinburgh to join the group of Prof. Guy C. Lloyd-Jones FRS as a post-doctoral researcher.

Current Research Interest

The catalytic nucleophilic trifluoromethylation of carbonyls was originally reported in the late 1980's[1] and is now routinely used for the preparation of trifluoromethylated compounds.[2] The most widely utilised nucleophilic trifluoromethylating reagent is $TMSCF_3$ (Ruppert-Prakash reagent), owing to its stability and ease of handling.[2] Despite its widespread use detailed mechanistic understanding of the reactivity of this reagent is currently limited.[2] This work describes a kinetic study of the reaction between $TMSCF_3$ and carbonyl compounds with a range of anionic catalytic initiators. This study has taken advantage of a range of new reaction monitoring technologies included stopped-flow IR and NMR for the *in situ* analysis of these rapid trifluoromethylation reactions.[3]

- Mechanistic Studies of Catalytic Nucleophilic Trifluoromethylation of Carbonyls



- Studied by ^{19}F NMR, stopped-flow NMR and IR
- Order Analysis Hammett Correlations
- Kinetic Modelling Cation Dependency

References:

1. G. K. S. Prakash, R. Kirishnamurti, G. A. Olah, *J. Am. Chem. Soc.* **1989**, 111, 393-395
2. X. Liu, C. Xu, M. Wang, Q. Liu, *Chem. Rev.* **2015**, 115, 683-730
3. C. P. Johnston, T. H. West, R. E. Dooley, G. C. Lloyd-Jones, *Unpublished Results*

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ARYLOXIDE-FACILITATED CATALYST TURNOVER IN α,β-UNSATURATED ACYL AMMONIUM CATALYSIS

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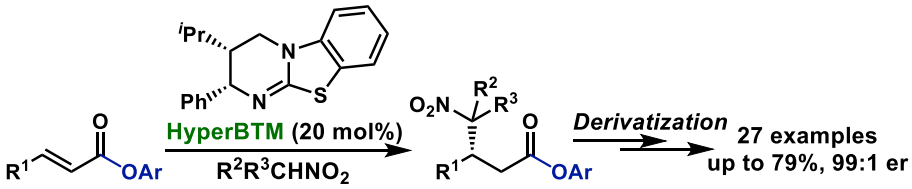
Author's Biography

Mark obtained an MChem at the University of Sheffield in 2010 before beginning his PhD at the University of Bristol as part of the Bristol Chemical Synthesis DTC. Mark started working with Dr Steve Thomas in 2011 on iron-catalyzed hydrofunctionalization of alkenes and alkynes, and moved with Steve to the University of Edinburgh in 2012 to complete his PhD. Since April 2015, Mark has been working with Prof. Andy Smith at the University of St. Andrews on Lewis base-catalyzed enantioselective transformations.

Current Research Interest

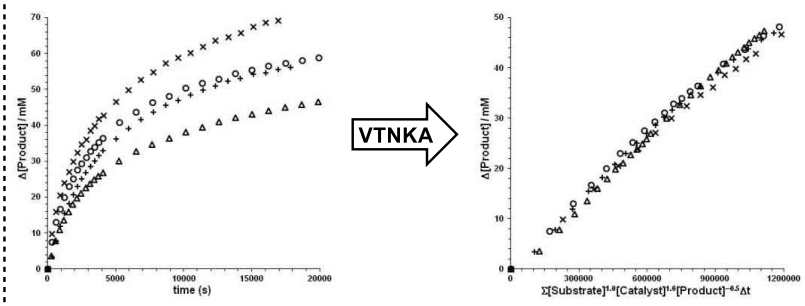
A new general concept in α,β-unsaturated acyl ammonium catalysis has been developed which uses aryloxide release from an α,β-unsaturated aryl ester substrate to facilitate catalyst turnover.[1] This method has been applied for the enantioselective isothiourea-catalyzed Michael addition of nitroalkanes to α,β-unsaturated *p*-nitrophenyl esters. The reaction mechanism has been probed through crossover studies, catalyst labeling and kinetic analysis.

This presentation will introduce the general concept behind aryloxide-facilitated catalyst turnover and focus on how mechanistic studies, in particular a recently-reported graphical method for kinetic analysis (variable time normalization kinetic analysis, VTNKA),[2] were used to provide fundamental insights about this process.



- *Isothiourea catalyst (HyperBTM) controls enantioselectivity*
- *Aryloxide facilitates catalyst turnover*

Graphical Kinetic Analysis:



Component orders: Substrate: 1 Catalyst: 1 Product 0.5

References:

1. A. Matviitsuk, M. D. Greenhalgh, D.-J. B. Antúnez, A. M. Z. Slawin, and A. D. Smith, *Angew. Chem. Int. Ed., manuscript accepted.*
2. J. Burés, *Angew. Chem. Int. Ed.* 2016, **55**, 2028-2031.

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STUDYING THE MECHANISM OF C-O CLEAVAGE IN LIGNIN MODEL COMPOUNDS BY RUTHENIUM-XANTPHOS CATALYSTS

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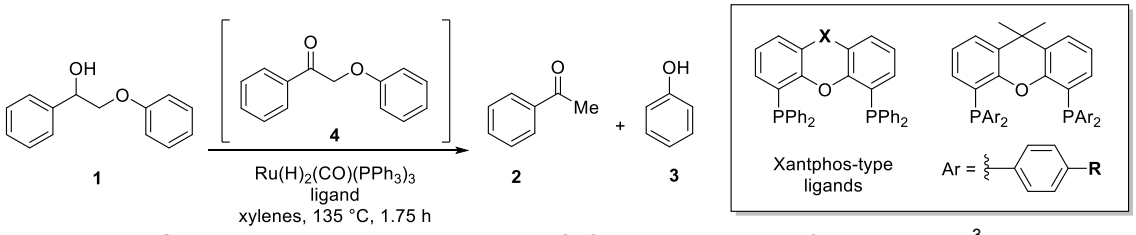
Author's Biography

I completed my MChem degree at the University of Edinburgh in 2011 which included a year-long placement at Macfarlan Smith (Johnson Matthey, Edinburgh) as an industrial process chemist. I then completed my PhD at the University of St Andrews in 2015, under the supervision of Dr Matthew Clarke in collaboration with Eastman Chemical Company, on the design of new catalysts for rhodium-catalysed hydroformylation. Since January 2016 I have been a post-doctoral researcher in the group of Prof. Paul Kamer, focusing on clean catalysis for sustainable development.

Current Research Interest

Lignin is an aromatic non-ordered polymer that gives plants their structural rigidity by acting as a resin. Lignin-based biomass is considered as one of the most promising resources for the sustainable production of energy and chemicals.[1] Due to the unique and complicated structure of lignin, simplified model compounds are tested in catalysis.[2] For example, 2-phenoxy-1- phenylethanol (**1**) mimics the β-O-4 linkage, which is the most commonly found linkage in lignin.



Scheme 1: Ruthenium-catalysed C-O bond cleavage of model lignin.[3]

Using a variety of Xantphos-type diphosphine ligands, we investigated the effect of the bite-angle (changing **X**) and electronic properties (changing **R**) of the ligands, on the cleavage of the lignin model substrate **1**.[3] It was found that the optimum bite angle was 111°, as both smaller and larger bite angles gave lower reactivity. Electron-donating groups (**R** = OMe) were also demonstrated to give enhanced catalytic activity, whereas electron-withdrawing groups led to a decrease. This indicated that the rate determining step may be the oxidative addition of the substrate to the metal center, due to the stabilisation of higher oxidation states by more sigma donating ligands, and was confirmed by further kinetic studies.

A number of *in situ* studies are also currently ongoing to determine different ruthenium species throughout the catalytic cycle. This is achieved using ^{31}P and ^{1}H NMR to show changes in the catalyst complex throughout the reaction.

References:

1. J. Zakzeski, P. C. A. Bruijnincx. A. L. Jongerius, B. Weckhuysen, *Chem. Rev.*, **2010**, 110, 3552-3599.
2. J. M Nichols, L. M. Bishop, R. G. Bergman, J.A. Ellman, *J. Am. Chem. Soc.*, **2010**, 132, 12554-12555.
3. L. Shaw, D. M. Upulani K. Somisara, R. C. How, N. J. Westwood, P. C. A. Bruijnincx, B. M. Weckhuysen, P. C. J. Kamer, *Catal. Sci. Technol.*, **2017**, 7, 619-626.

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Towards the rational design of isoform-selective Cyclophilin ligands

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Author's Biography

Dr Alessio De Simone carried out his PhD in Drug Discovery at the Italian Institute of Technology working on a novel class of molecules for the treatment of nicotine addiction and compulsive behaviour under the supervision of Dr Bottegoni and Prof Cavalli. During his PhD, he joined the group of Prof Brennan at the Structural Genomic Consortium in Oxford, where he worked on the synthesis of novel bromodomain ligands. After his PhD, he moved to Edinburgh to join Dr Hulme's and Dr Michel's groups as a Postdoctoral research associate, working on the design and the synthesis of selective cyclophilins ligands. His research interests cover drug discovery and medicinal chemistry, with a particular focus on the rational design and synthesis of novel chemical entities with promising pharmacological activity.

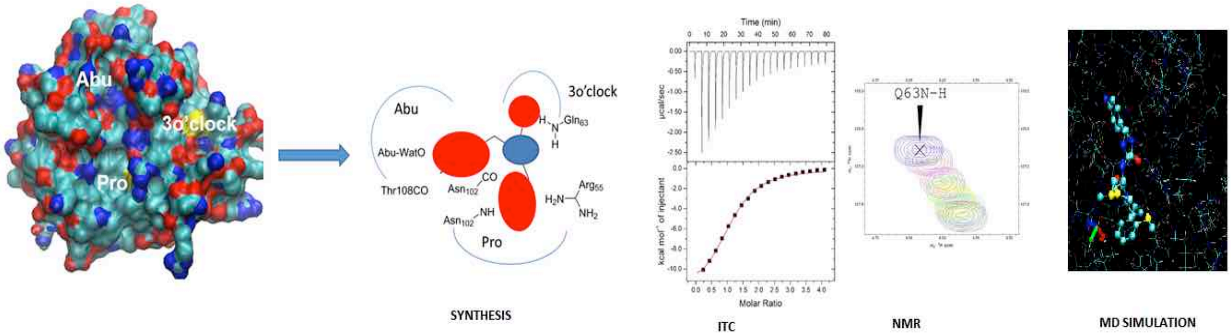
Current Research Interest

Cyclophilins are folding helper enzymes belonging to the class of peptidyl prolyl cis-trans isomerases. They catalyze the cis-trans isomerization of peptidyl prolyl bonds in unfolded and native proteins[1], playing a pivotal role in a multitude of cellular functions like cell growth, proliferation, and motility. The selective inhibition of these enzymes by different ligands could represent a compelling strategy for the treatment of various pathologies, such as viral infections and cancer[2] and can provide a better understanding of the physiological role of the various cyclophilins in the human body.

We have setup a platform that combines computational analyses, organic synthesis, structural studies, biophysical and in vitro assays in order to understand how existing ligands interact with different Cyclophilins. Our overall objective is to delineate design principles for isoform-selective Cyclophilin inhibition, and to develop new cyclophilin ligands with desirable binding affinity and selectivity profiles.

A novel class of compounds, designed following a 'three-vector' strategy, is pursued to enable interactions with two conserved Abu & Pro pockets, and a less conserved remote 3o'clock pocket. (See Scheme). Some of the synthesized derivatives show a promising binding profile on CypA, paving the way for the development of more potent and isoform-selective ligands.

Scheme:



References:

1. "Cyclophilin and peptidyl-prolyl cis-trans isomerase are probably identical proteins". Fischer et al. *Nature*, *337*, 476–478, **1989**.
2. "Isoform-Specific Inhibition of Cyclophilins". Daum et al. *Biochemistry*, *48*, 6268–6277, **2009**.

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Single-molecule transmembrane supramolecular chemistry

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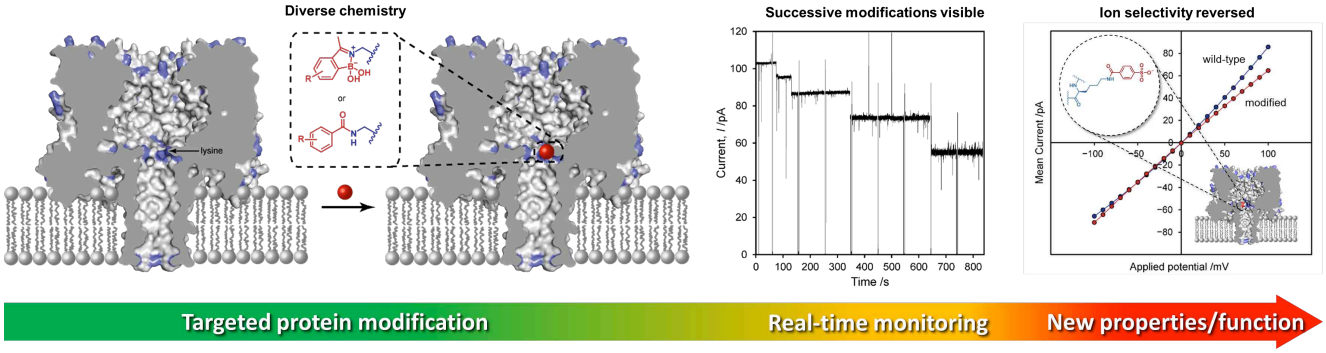
Author's Biography

I obtained my Ph. D. on nanoparticle assembly from the University of St Andrews under the supervision of Dr Euan Kay. This excellent grounding in supramolecular chemistry led to my current post-doctoral position at the University of Edinburgh in the group of Dr Scott Cockroft, where I am currently engaged in exciting projects relating to single-molecule transmembrane supramolecular chemistry and the development of transmembrane molecular machines.

Current Research Interest

Monitoring the ion current flow through a single nanopore has proved to be a powerful technique for the *in situ*, non-destructive visualisation of molecular structure, binding and reactivity.[1] Proteins, such as α-hemolysin (α-HL), provide atomically precise structures which have been successfully employed as nanopores for sensing, sorting and even as platforms for the construction of trans-membrane molecular machines.[2] Here, the *in situ* post-translational synthetic modification of a wild-type α-HL nanopore is demonstrated as a simple, efficient and robust alternative to genetic modification or native chemical ligation[3] – techniques demanding of time and expertise – for the construction of sophisticated nanopore sensors and devices.



Single-molecule visualisation of reversible dynamic covalent iminoborate formation with lysine residues of the protein allows for characterisation of the reactive sites and subsequent, irreversible amide formation enables the targeted and controlled functionalisation of the nanopore. Ultimately, we envisage the development of a simple and robust synthetic toolkit for the modification of nanopores, with well-defined and well-understood reactivity.

References:

1. H. Bayley, P. S. Cremer, *Nature* **2001**, 413, 226–230.
2. M. A. Watson, S. L. Cockroft, *Chem. Soc. Rev.* **2016**, 45, 6118–6129.
3. J. Lee *et al.* ACS Nano **2016**, 10, 8843–8850.

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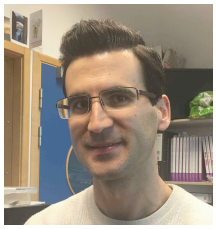
CAPSULES FOR MOLECULAR RECOGNITION AND CATALYSIS



Author: Vicente Martí-Centelles
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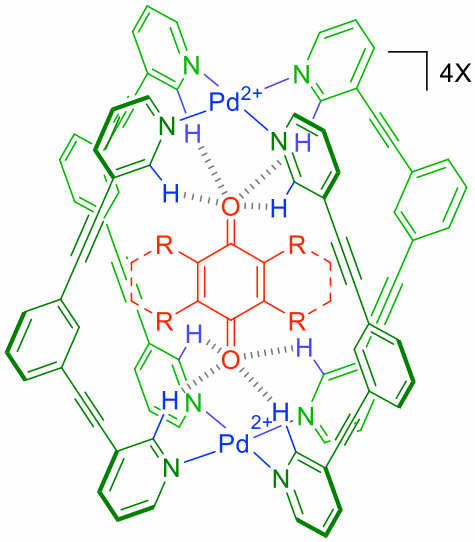
Author's Biography

Dr. V. Martí-Centelles graduated in Chemistry with honors in 2007 (Univ. Jaume I, Spain). He got a Spanish Ministry of Education grant to develop his PhD on new pseudopeptidic macrocyclic hosts for molecular recognition under the supervision of Profs. S.V. Luis and. M.I. Burguete at Univ. Jaume I with two research stays with C. Cativiela (Univ. Zaragoza) and R. Vilar (Imperial College London). He received his PhD with honors in 2012. He got a postdoctoral grant from the Generalitat Valenciana in 2013 to work at Univ. Jaume I (Prof. S.V. Luis), Oxford Univ. (Prof. P.D. Beer) and the company Biotica (Legionella detection). He joined the Lusby research group at Univ. of Edinburgh in 2015.

Current Research Interest

Dr. V. Martí-Centelles research interests are focused on the design and synthesis of self-assembled host systems for molecular recognition and catalytic applications. Our current attention has been aligned with simple Pd_2L_4 capsule systems, such as $\mathbf{1}^{4+}$ (Figure 1), where encapsulation of p-quinone-type guest ($\mathbf{G}^{n}$) has been achieved by promoting complementary interactions that exist with the inherently polarized metallo-organic scaffold.[1] This type of binding also results in modulation of the guests' electronic properties, [1] which we now show can be exploited for catalytic applications. wherein capsule-bound dienophiles are activated for Diels-Alder (DA) reactions. Not only does this approach reveal high activity (k_{cat}/k_{uncat} > 10^3), it also overcomes the product inhibition problems that have become synonymous with supramolecular cycloaddition catalysis, with TONs >1000 feasible. A detailed analysis of the catalysed process also reveals features reminiscent of biological systems, wherein multiple weak interactions promote selective stabilisation of the transition state. We will also show that this system can modulate the intrinsic chemo, regio, site and diasteroselectivity of several DA reactions, which is often difficult or impossible to achieve using conventional small-molecule catalyst approaches.



$[\mathbf{G}^{n} \subset \mathbf{1}]\cdot 4X$

X = OTf or BArF

Figure 1. A $Pd_2L_4^{4+}$ cage-quinone host-guest

References:

1. D. P. August, G. S. Nichol, P. J. Lusby, *Angew. Chem. Int. Ed.* **2016**, *55*, 15022–15026.

Oral Abstracts

Stream B Talks

Physics Theatre C

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PUMP-PROBE SIMULATION OF CS2 AND CHD: TIME-DEPENDENT PHOTOIONIZATION

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Author's Biography

I have defended my master thesis at Moscow Institute of Physics and Technology in the field of plasma physics and chemistry. I completed my Ph.D. at the University of Hannover in atomic, optical and molecular physics investigating strong laser field interaction with model systems. At the University of Edinburgh, I am studying photochemical reactions involving weak and strong laser fields with different wavelengths.

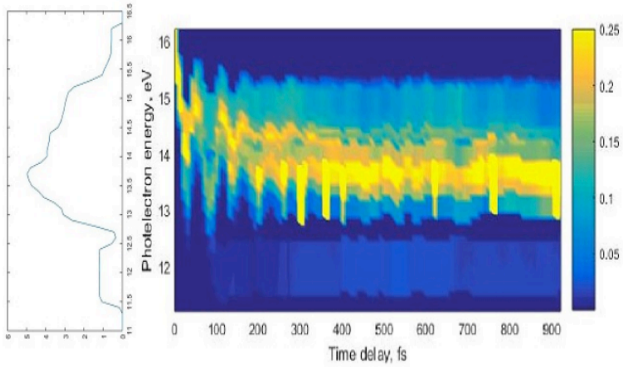
Current Research Interest

We are reporting a new tool for analyzing a pump-probe experiment involving molecular excitation and photoionization. The photoelectron spectrum is a function of time and quantum molecular dynamics. We used Dyson Orbitals (DO)-based approach calculating to find the ionization rate. We consider 1,3-cyclohexadiene (CHD) and carbon disulfide (CS_2). The former exhibits ring opening and can be considered prototypical for a range of photochemical reactions. The latter is important as a synthesis intermediate for carbon tetrachloride, used in cellophane production or as an insecticide, and other applications.

For CHD, we make use of previously calculated reaction trajectories and their relative weight to find out which scenario is the most probable, and how the total photoionization spectrum looks like.

A lot remains unknown if CS_2 is not in its equilibrium state at the moment of ionization. We conduct accurate *ab initio* simulations[2] of the pump pulse and introduce the concept of the "average trajectory" for the dissociative and non-dissociative scenario.

We find that the photoionization spectrum allows to judge about structural changes in molecules and electron structure changes.



CS_2 photoelectron spectrum

References:

1. G. R. Cook and M. Ogawa, *J.Chem.Phys.* **1969** 51, p. 2419
2. D. Bellshaw, D. A. Horke, A. D. Smith, H. M. Watts, E. Jager, E. Springate, O. Alexander, C. Cacho, R. T. Chapman, A. Kirrander, and R. S. Minns, *Chem. Phys. Lett.* **2017**
3. S. Gozem, A. O. Gunina, T. Ichino, D. L. Osborn, J. F. Stanton, and A. I. Krylov, *J. Chem. Phys. Lett.* **2015** 6 p. 4532

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ADOR SYNTHESIS REALIZED BY USE OF THE HYDROSTATIC PRESSURE

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Author's Biography

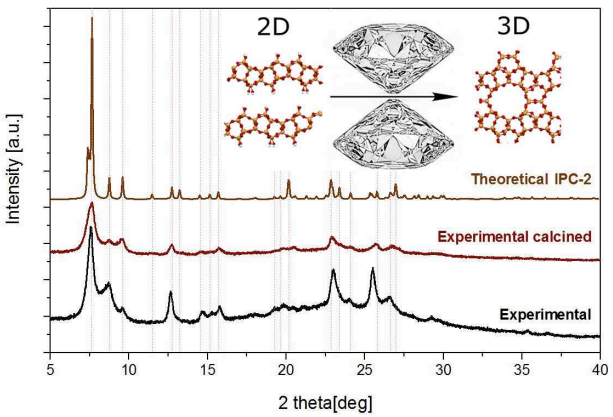
I received my master degree in Chemistry from Jagiellonian University in Cracov, Poland. Then, I joined the Department of Synthesis and Catalysis in J. Heyrovsky Institute of Physical Chemistry in Prague, Czech Republic, where I completed my PhD in 2016 under the supervision of Prof. Jiří Čejka.

Currently, I hold the postdoctoral position at the University of St Andrews in Prof. Russell Morris's group. My research is focused on the synthesis, post-synthesis modification, and application of various materials, especially 2D zeolites. I am also interested in characterization methods, mainly X-ray diffraction and TEM imaging of materials.

Current Research Interest

Conventional zeolites have been recognized as 3D tetrahedrally-connected frameworks however some of them are also known to exist in various 2D layered forms. Recently, the hydrolysis of UTL germanosilicate to layers (IPC-1P) has started the new branch in 2D zeolites chemistry. Modifications of the layered precursor IPC-1P led to the discovery of novel, 3D zeolites i.a. IPC-4 (PCR) and IPC-2 (OKO) [1]. This novel approach, called ADOR (Assembly-Disassembly-Organization-Reassembly) is an alternative way of zeolite synthesis, more tunable than conventional solvothermal method.

Recently, Jorda et.al. showed a new way of zeolite transformation so called pressure-induced reconstructive phase transition process [2]. It was performed using diamond anvil cell (DAC) device which allows bringing material under high pressure (up to hundreds GPa). Herein, we present the very first transition of layered zeolite precursor (IPC-1P) into 3D zeolite IPC-2 (OKO) using hydrostatic pressure.



Using DAC device under the pressure of 1 GPa at 200 °C the IPC-1P was transformed into IPC-2 zeolite. Calcination of transformed phase showed stability of the obtained zeolite. The further investigation have shown that the temperature and pressure of treatment have significant influence on the structure of final material.

In principle, this approach can be used for preparation of other ADOR zeolites. Moreover, theoretical calculations have shown that this method is likely to produce the structures with higher framework energies. Thus, there is high possibility that hydrostatic pressure could be a way to get hydrothermally unfeasible zeolites.

References:

1. Eliašová P., Opanasenko M., Wheatley P.S., Shamzhy M., Mazur M., Nachtigall P., Roth W.J., Morris R.E., Čejka, J., Chem. Soc. Rev. **2015**, 44, 7177-7206
2. Jorda J.L., Rey F., Sastre G., Valencia S., Palomino M., Corma A., Segura A., Errandonea D., Lacomba R., Manjon F.J., Oscar Gomis, Kleppe A.K., Jephcoat A.P., Amboage M., Rodriguez-Velamazan J.A., Angew. Chem. Int. Ed. **2013**, 52, 10458 –10462

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Manipulation of Polar Order in Ferroelectric 'Empty' Tetragonal Tungsten Bronzes

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Author's Biography

After completing an MSci in chemistry at the University of Glasgow, I completed my PhD under the supervision of Dr Finlay Morrison at the University of St Andrews working on ferroelectrics with the tetragonal tungsten bronze structure. After finishing my PhD, I was employed as a research assistant in Prof. Jim Scott's research group, characterizing ferroelectric and multiferroic compounds. I have recently been appointed as a Research Fellow in ferroic materials working jointly in the Morrison and Scott research groups.

Current Research Interest

The tetragonal tungsten bronze (TTB) structure, $A1_2A2_4B1_2B2_8C_4O_{30}$, consists of a corner-sharing network of BO_6 octahedra with 3 types of 'tunnel' sites. Distortion of the aristotype TTB structure is common due to octahedral tilting to relieve A-site-generated strain and results in superstructures and incommensurate modulations. These, often subtle, structural modifications influence whether ferroelectric (FE), relaxor-ferroelectric (RFE) or dipole glass behaviour is observed.[1] Altering the size of the A-site cations sizes, *via* doping, allows a degree of control over the structure and therefore the properties. A-site vacancies may be introduced while doping to maintain charge balance.[2] This present work focuses on such a family of TTBs with an unusually large number of A-site vacancies (> 1/5 of A-sites are unoccupied).[3,4] Starting from the normal ferroelectric $Ba_4Dy_{0.67}\square_{1.33}Nb_{10}O_{30}$ ($\square$ = vacancy), doping is shown to disrupt polar order, resulting in a decrease in the ferroelectric Curie temperature, T_C. This is shown to originate from structural changes as observed from powder x-ray diffraction (PXRD) and powder neutron diffraction (PND) data.

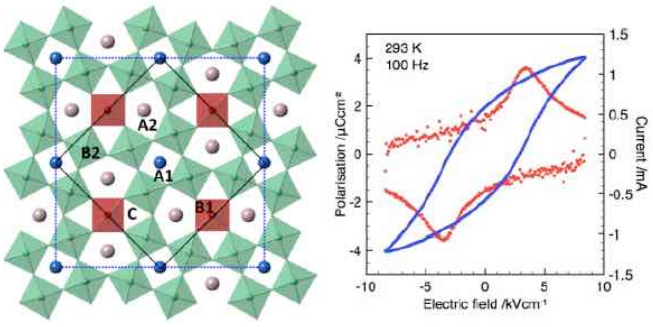

Figure 1: (a)TTB structure showing unit cells of tetragonal aristotype (black) and simple orthrhombic superstructure (blue); (b) ferroelectric polarisation-electric field loop and associated current switching.

References:

1. X. Zhu, M. Fu, M. C. Stennett, P. M. Vilarinho, I. Levin, C.A. Randall, J. Gardner, F.D. Morrison, and I. M. Reaney, *Chem. Mater*. **2015**, 27, 3250.
2. K. Masuno, *J. Phys. Soc. Jpn*. **1964**, 19, 323.
3. J. Gardner and F. D. Morrison, *Dalton Trans*. **2014**, 43, 1168.
4. J. Gardner and F. D. Morrison, *Appl. Phys. Lett*. **2016**, 109, 072901.

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SYNTHESIS OF MAGNETIC POLYHEDRA: CUBES AND TRIANGULAR BIPYRAMIDS

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Author's Biography

My interests lie within the field of Inorganic Chemistry, Molecular Magnetism and Supramolecular Chemistry. During my PhD and postdoctoral positions I have worked on gold, ruthenium and iridium chemistry, and have synthesised new single-molecule magnets, magnetic coolers, magnetic spin switches and spin-frustrated materials. Currently I am merging Molecular Magnetism and Supramolecular Chemistry; designing and studying magnetic materials based on metallosupramolecular architectures.

Current Research Interest

The disciplines of Supramolecular Chemistry and Molecular Magnetism can both be considered of high impact, however, examples of the amalgamation of the two are still rare. Merging these two important areas will enable me to build hybrid magnetic materials that have potential application in spintronics, information storage and data manipulation, drug delivery, stabilisation of reactive molecules and catalysis. Coordination-driven self-assembly through the use of strong and directional metal-ligand bonds has been exploited in Supramolecular Chemistry for the construction of 0-3D cages, capsules and porous polymeric materials. The interest in these structures primarily stems from host-guest chemistry, with potential application in catalysis, drug delivery and the stabilisation of reactive intermediates.[1] Although the design of these systems has been extensively studied with diamagnetic metals, only a few examples employing paramagnetic metal ions have ever been reported.[2] Herein I discuss the structures and magnetic properties of heterometallic cages built through the use of pre-made paramagnetic metalloligands and paramagnetic linker units with the appropriate directionality and angularity to access a range of magnetic cages (cubes and triangular bipyramids) capable of hosting magnetic guests that will have the potential to exhibit tunable (e.g. switchable) magnetic properties.

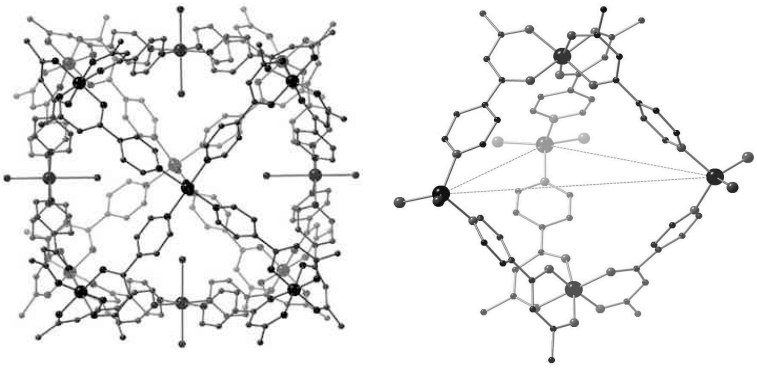

Figure 1. From left to right, examples of molecular structures of magnetic $[Cr_8Co_6L_{24}Cl_{12}]$ cube and $[Fe_2Co_3L_6Cl_6]$ trigonal bipyramid, where HL is 1-(4-pyridyl)butane-1,3-dione.

References:

1. R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, **2011**, 111, 6810-6918, and references therein
2. S. Sanz, H. M. O'Connor, V. Marti-Centelles, P. Comar, M. B. Pitak, S. J. Coles, G. Lorusso, E. Palacios, M. Evangelisti, A. Baldansuren, N. F. Chilton, H. Weihe, E. J. L. McInnes, P. J. Lusby, S. Piligkos and E. K. Brechin, *Chem. Sci.*, **2017**, Advanced Article, DOI: 10.1039/C7SC00487G, and references therein

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Structure and reactivity of Cu-doped Au(111) surfaces

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I obtained a chemistry degree in 2001, form the University of Padua, Italy, with a dissertation focused on the catalytic activity of the surfaces of metal oxides. I was awarded a PhD in Surface Science in 2007, from Cardiff University (Prof. M. Bowker), focusing on the surface chemistry of model systems related to automotive exhaust catalysis. In 2007 I moved to St Andrews as a Research Fellow (Prof. N. V. Richardson), working on the self-assembly of organic molecules of technological interest at metal surfaces. My current research (Prof. C. J. Baddeley), focuses on the catalytic activity of Cu/Au systems towards coupled dehydrogenation/hydrogenation reactions.

Ultra-thin atomic layers on single crystal metal surfaces can provide structurally interesting systems in which a delicate balance of forces arises from the adsorbate - substrate lattice mismatch. The resulting interfacial layers are generally stressed and tend to minimize the excess energy via surface reconstruction. The Cu/Au(111) system has received the attention of many studies, only a few however have been performed in an ultra-high vacuum (UHV) environment, using surface sensitive techniques.

In this contribution, the room temperature deposition of copper onto the (22×√3)-Au(111) surface is investigated using scanning tunnelling microscopy (STM). Initially, preferential adsorption/incorporation into alternate herringbone elbows is observed (Fig. 1a).[1] With increasing coverage, a critical cluster size is reached above which copper-rich islands exhibit a reconstructed surface reminiscent of the clean Au(111) herringbone reconstruction (Fig. 1b).[1-3] Disordered, pseudo-ordered and ordered surface layers are observed. Models for the initial adsorption/incorporation mechanism and ad-layers formation and evolution are discussed qualitatively in terms of surface strain within the gold and copper layers. Further, the reactivity of Cu-doped Au(111) systems is considered in light of their catalytic applications and towards the adsorption of organic molecules of interest in nanotechnology.

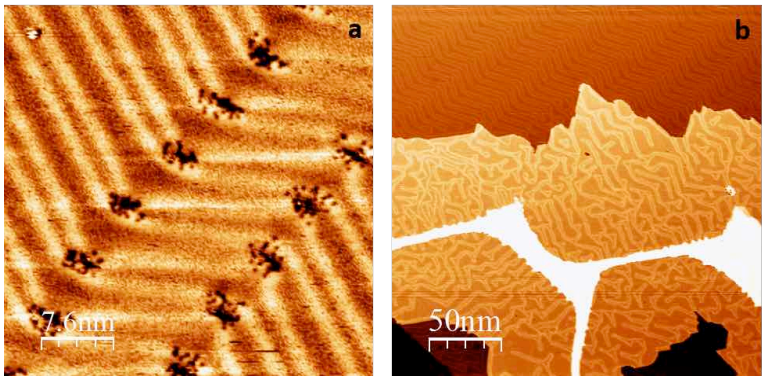

Fig. 1: a) Cu adsorption at Au(111) herringbone elbows, *ca.* 0.02 ML, -1.0 V, 0.78 nA; b) reconstructed copper-rich layer, *ca.* 0.75 ML, -1.1 V, 1.0 nA.[1]

References:

1. F. Grillo *et al.*, *New J. Phys.* **2011**, 13, 013044;
2. T. Trimble *et al.*, *Phys. Rev. Lett.* **2005**, 95, 166106;
3. L. Wang *et al.*, *J. Phys. Chem. C* **2017**, 121, 7977-7984.

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DEVELOPMENT OF PEPTIDE-BASED ELECTROCHEMICAL BIOSENSORS

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Author's Biography

Eva obtained her BSc degree in Chemistry from the University of Oviedo (Spain) in 2007, and her PhD degree in 2012 from the same university where she worked on the development of nucleic acid-based electrochemical biosensors. She moved to Scotland to work in the development of commercial electrochemical biosensors at Alere, a leading global company in the development of medical devices and diagnostics tools. In January 2014 after 18 months working in the industry sector, she moved to the University of Edinburgh to join Prof. Bradley's group as a postdoctoral researcher where she is currently working in the development of electrochemical sensors for implantable microsystems for personalised anti-cancer therapy (IMPACT project).

Current Research Interest

My current research is focused in the development of electrochemical, peptide-based biosensors for the detection of proteases and analysis of physiological parameters. These are interesting targets due to their relevance in many pathophysiological conditions, including inflammation and cancer. In order to develop selective and sensitive tools for the detection of these enzymes the use of redox-tagged peptides, tethered to a gold surface through self-assembled monolayers (SAM) has been developed.

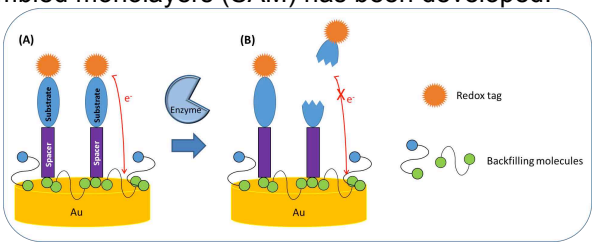

Figure 1. Principle of electrochemical detection. (A) Sensing phase consisting of a mixed self-assembled monolayer containing a redox-tagged peptide. (B) Cleavage of the substrate by the enzyme under interrogation.

This platform was used to investigate redox-tagged peptides as sensing platforms for the detection of various proteases such as trypsin [1] and human neutrophil elastase (HNE). The synthesised peptide-based probes consisted of a short peptide sequence specific for the relevant enzyme, but modified with both a redox tag and a thiol-containing moiety, which allowed electrochemical detection and immobilisation onto a gold surface, respectively. The addition of the enzyme causes a displacement or removal of the electrochemical label and a change in the resultant electrochemical signal (Figure 1).

Systematic optimisation of the proposed platform was been carried out, including an analysis of:
(i). Different redox tags; (ii). Various spacers (nature and length) between the anchor moiety (cysteine) and peptide sequences; (iii). Numerous modes of surface attachment (e.g. single, dual or triple thiol anchors) were evaluated in terms of sensor performance; (iv). Monolayer deposition.

The influence of each of these "design parameters" on sensor performance will be discussed. In summary, a new, robust, electrochemical sensor for the detection of proteases has been developed.

Acknowledgments - Implantable Microsystems for Personalised Anti-Cancer Therapy is an EPSRC funded grant (Ref. EP/K034510/1).

References:

1 E.González-Fernández, N. Avlonitis, A. F. Murray, A. R. Mount, M. Bradley, Biosen. Bioelectron. **2016**, 84 82-88.

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IN-SITU THERMAL BATTERY DISCHARGE USING NiS_2 AS A CATHODE MATERIAL

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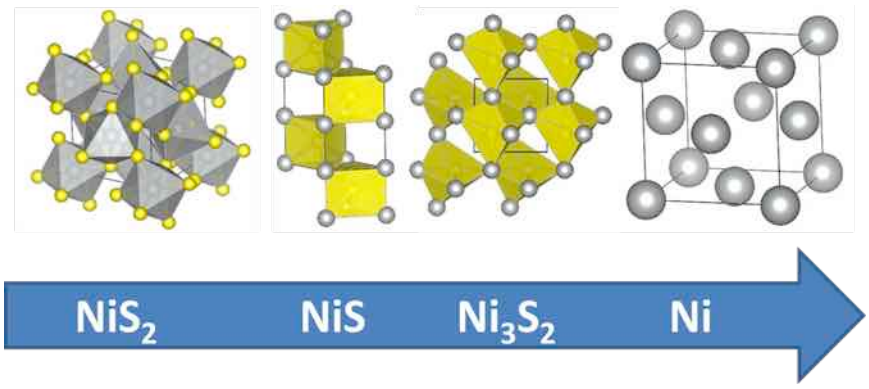
Author's Biography

Julia completed her undergraduate studies at the University of Warwick. This was followed by a PhD and approximately 1 year PDRA in the group of Dr Ivana Evans at Durham University. During this time she spent some time at the Institut Laue-Langevin in Grenoble, France. Julia then moved to the University of Liverpool, where she spent two years working for Prof. Matt Rosseinsky. In 2014 Julia joined the group of Prof. John T.S. Irvine in St Andrews. Julia has close links with central facilities such as the ISIS neutron source, Diamond Light Source and the Spallation Neutron Source (USA).

Current Research Interest

Thermal batteries are primary batteries which find uses in applications such as emergency power supplies in aircraft, which require a constant power to be drawn from the battery over a length of time. Typically, these batteries consist of a lithium-containing anode, a molten salt electrolyte, a separator and a cathode, which is often a sulfide. NiS_2 (along with FeS_2 and CoS_2) are some of the most widely studied cathode materials, but the existing literature has largely focussed on characterisation of these cathodes using electrochemical techniques. Due to the high temperature operation of the battery, it has been difficult to obtain a full crystallographic understanding of the phases which occur during discharge and at device operating temperature.

Here we report the first combined *in-situ* neutron diffraction and battery discharge experiment carried out on a thermal battery, using NiS_2 as the cathode material. This experiment used a specially designed sample environment for the POLARIS diffractometer. We have probed the evolution of the crystalline phases present during discharge and used quantitative Rietveld refinement to link the phase percentage to the voltage observed in the battery discharge profile. This has led to the proposal of a new discharge mechanism for NiS_2 when used as a cathode in thermal batteries.[1]



References:

1. J. L. Payne, J. D. Percival, K. Giagloglou, C. J. Crouch, G. M. Carins, R. I. Smith, R. Comrie, R. K. B Gover, J. T. S. Irvine, *ChemElectroChem*, **2017**, 4, 1916-1923

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WHITHER CRYSTALLOGRAPHY… A VIEW FROM THE GROUND

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David did both his undergraduate degree and PhD at the University of Otago, New Zealand (2006) working with Prof. Lyall Hanton on the synthesis and characterization of coordination polymers. Postdoctoral positions proceeded from this; with Prof. Robin Rogers at the University of Alabama (2007), Prof. Paul Lickiss at Imperial College London (2008-2009), and Prof. Alex Slawin at the University of St Andrews (2010-2012). This was followed by a period running the X-ray diffraction lab at Texas Tech University (2012-2013), before returning to St Andrews to help run the small-molecule crystallography lab and service in September 2013.

David's research is focused on the determination of molecular structure by single crystal X-ray diffraction, along with the practical routine of running an X-ray structure determination service within an academic setting. This includes the necessity of chemical knowledge across a range of sub-disciplines in order to be able to correctly interpret what is going on within a structure. As well as this, David retains an interest in metallosupramolecular chemistry.

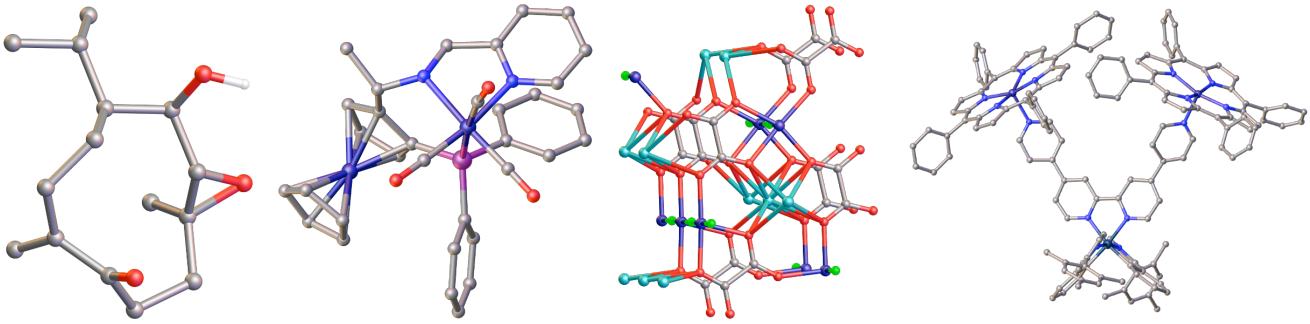

Figure 1. Views illustrating some of the range of structures from varying sub-disciplines of chemistry determined in a crystallography service

The role of X-ray structure determination within an academic setting has changed over the years; starting as an area of research in its own right, before becoming a routine analytical technique in many cases. This is mostly due to the advances in the technology associated with single-crystal X-ray diffraction, and the resulting wider accessibility of the technique to the non-specialist. However, other developments are leading to new areas of crystallographic research that would not have been previously possible. A personal overview of how I ended up in an academic crystallographic position will be presented, as well as an overview of where crystallography has been as a discipline, as well as where it may end up going.

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MOLECULAR MAGNETS UNDER PRESSURE

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Author's Biography

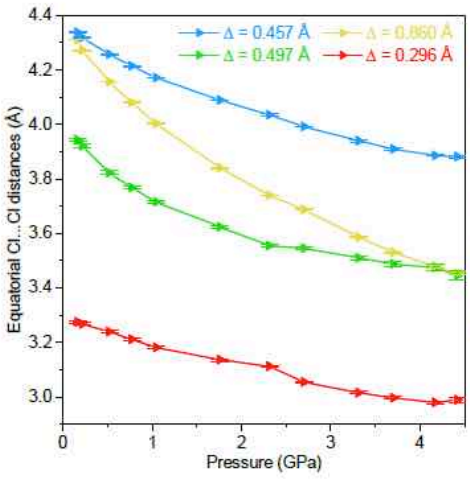
I am a physicist pretending to be a chemist. I completed my PhD in physics from Queen Mary, University of London in 2016 where I used neutron total scattering and the reverse Monte Carlo technique to model metal organic frameworks and multiferroics. I joined the Parsons' group in Edinburgh in 2017 and I now work on single crystal x-ray diffraction on molecular magnets under pressure.

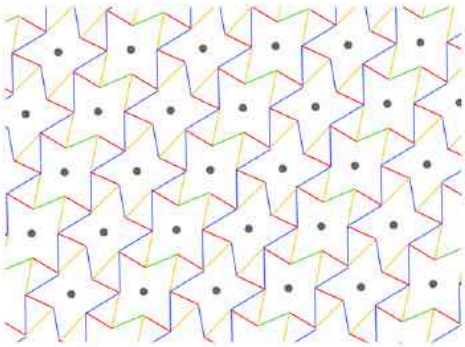
Current Research Interest

Current information storage technologies depend on the ability of storage media to retain a magnetic moment after removal of an applied field. Single molecule magnets, which utilise highly anisotropic transition metal and lanthanide ions and ligands than enhance their anisotropy are an exciting development in the search for denser storage media.

Here we use high pressure crystallography both to change and measure molecular geometries[1] to probe the structure-property relations of molecular magnets. In the series of materials I am investigating, hexahalorhenates, the magnetic exchange depends on the ability of the metal electrons to be transferred to the ligand, and on the X···X and X···π···X distances[2]. Therefore subtle structural changes can lead to significant enhancement of the magnetic properties.

I will discuss the techniques used in high pressure crystallography, how it differs from its single crystal counterpart and give examples of analysis performed on two molecular magnets.





References:

1. Woodall, C. H,: et al. Nat. Commun. **2016**, 13870
2. Figgis, B. N.; Lewis, J.; Mabbs, F. E. *J. Chem. Soc.* **1961**, 3138.

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DIFFERENCE IN REACTIVITY OF TWO ZINC BINDING PLANT METALLOTHIONEINS ISOFORMS

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I have completed my PhD under the supervision of Dr. Claudia Blindauer, Warwick University working on metal-cluster topology and cluster dynamics of two zinc binding metallothioneins isoforms. After completion of my PhD in November 2015, I have moved to Texas A&M university, USA for a post-doctoral training in the group of Dr. Tatyana Igumenova. My research was focused on studying the structural basis of Protein Kinase C (PKC) and Peptidyl prolyl isomerase (Pin1) binding and inhibition. Currently, I am joining as a post-doctoral research fellow in the group of Professor Paul Kamer /Professor Andrew Smith, University of St-Andrews, and Dr. Andrew Marr at Queen University of Belfast. I shall work on design artificial metalloenzymes by functionalizing protein with nitrogen/phosphorus ligands and will investigate the homogeneous catalysis properties for selective amination.

Current Research Interest

Metallothioneins are small cysteine rich protein. Type 4 metallothionein from dicotyledonous plant *Arabidopsis thaliana* has two seed specific isoforms-MT4a and MT4b. Both the isoforms contain 17 cysteines and 2 conserved histidines comprises 84% sequence similarity of 84 and 85 amino acid residues long protein chain respectively. The protein have been expressed in *E.coli* and purified proteins were found to bind six zinc[1] ions similar to their homolog E_C from monocotyledonous wheat.[2,3] Like E_C, MT4a and MT4b are found exclusively in reproductive tissue, and it is believed that these proteins release zinc to biomolecules or other proteins during seed germination to help seedling growth. Hence to get an insight of zinc transfer dynamics from these two isoforms; an attempt has been made to study zinc transfer from these protein isoforms to 4-(2-Pyridylazo) resorcinol (PAR), Ethylenediaminetetraacetic acid (EDTA) as a mimic of biomolecules and effect of pH variation on zinc release. Kinetic studies by UV-Visible spectroscopy revealed that MT4a transfers zinc to EDTA and PAR considerably faster than MT4b. Metal speciation by native Electrospray Ionisation Mass Spectrometry (ESI-MS) shows that both isoforms differ in metal transfer/release, forming different stable under-metalated species in a time-dependent manner. In addition, 1D ^{1}H and 2D [^{1}H, ^{15}N] HSQC NMR spectroscopies revealed that in both homologues, their two domains have markedly different reactivities. However, both domains of MT4a transfer/release zinc faster than MT4b domains.

Acknowledgement

Gratitude to my PhD supervisor Dr. Claudia Blindauer (Warwick University). Thanks to Professor Peter Goldsbrough (Purdue University, USA) for providing us the expression plasmid of MT4a and MT4b. The University of Warwick and department of Chemistry for scholarship to HTI. Advantage West Midlands and the European Regional Development Fund (Birmingham Science City) for support.

References:

1. O. I. Leszczyszyn, H. T. Imam and C. A. Blindauer, *Metallomics*, 2013, **5**, 1146-1169.
2. O. I. Leszczyszyn, R. Schmid and C. A. Blindauer, *Proteins: Struct., Funct., Bioinf.*, 2007, **68**, 922-935.
3. E. A. Peroza and E. Freisinger, *J. Biol. Inorg. Chem.*, 2007, **12**, 377-391.

Poster Abstracts

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NOVEL TRYPANOSOMATID INHIBITORS INSPIRED BY NATURE

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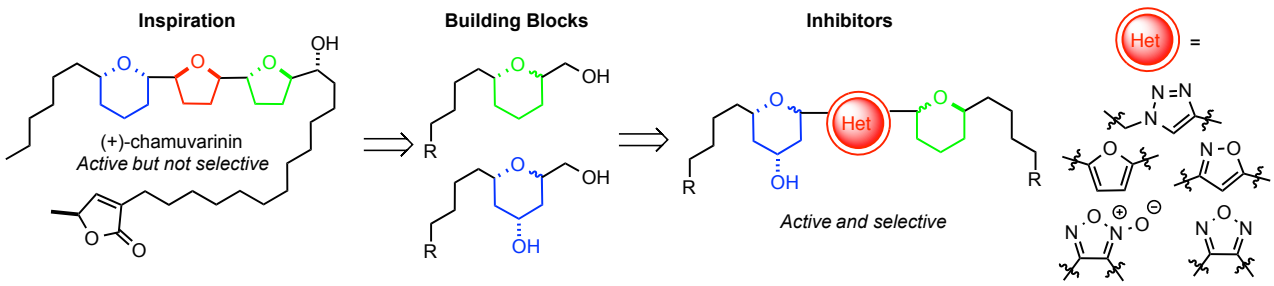
Author's Biography

I obtained my undergraduate degree from the University of Edinburgh in 2006 followed by a PhD in synthetic methodology with Prof. Andy Smith at the University of St Andrews. My PhD thesis was entitled 'Pyrazolidinones as Templates in Asymmetric Catalysis'. After a year postdoc with the Smith group, in 2013 I moved to the lab of Dr Gordon Florence and into a medicinal chemistry program (details below).

Current Research Interest

The Neglected tropical diseases African sleeping sickness, Chagas disease and Leishmaniasis, all caused by Trypanosomatid parasite infection, are an ongoing and increasing burden to human and animal health, having the most devastating effect on the world's poorest countries. A lack of financial incentive for pharmaceutical companies means there are few validated drug targets, while the currently prescribed treatments are antiquated and exhibit severe side effects.[1]

Chamuvarinin, an acetogenin isolated from the roots of *Uvaria chamae*, displays single figure micromolar activity towards one of these parasites. Inspired by chamuvarinin's central core, we have created modular enantiopure THP units that we can rapidly couple with different heterocycles to construct several new series of Trypanosomatid inhibitors, based on a general THP-heterocycle-THP format. These simplified structural analogues are toxic to our tested Trypanosomatid parasites at low micromolar levels, with several showing excellent selectivity over mammalian cells. This paper will detail our SAR studies in the five series tested to date as well as our efforts towards identifying the protein target(s) of these novel anti-parasitic agents.[2]



References:

1. World Health Organization, Switzerland, 2010: First WHO report on neglected tropical diseases: working to overcome the global impact of neglected tropical diseases.
2. G. J. Florence, T. K. Smith *et al.*, *ChemMedChem* **2014**, *9*, 2548-2556.

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Towards the Biochemical and Biophysical Characterisation of Serine Palmitoyltransferase: a Human ER Multienzyme Transmembrane Complex

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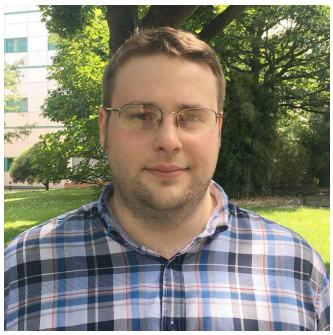
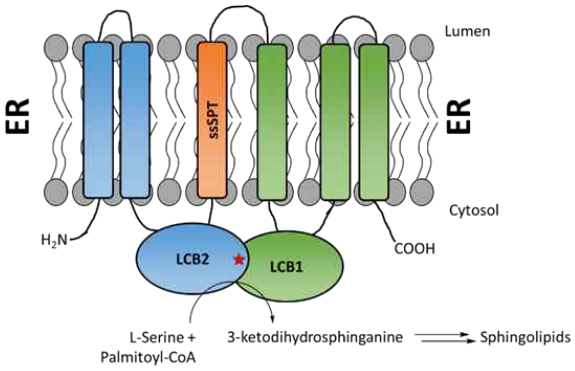


I obtained by MChem in Chemical Biology from the University of Warwick in 2011, working with Dr Christophe Corre on understanding the control of secondary metabolite biosynthesis in Streptomyces. Following this, I obtained my PhD from the same institution in 2015 under the supervision of Prof. Tim Bugg, studying the enzymology of a family of non-heme iron dioxygenases. I am now a PDRA in the group of Prof. Dominic Campopiano, biophysically and biochemically characterizing the human serine palmitoyltransferase enzyme.

Sphingolipids are key constituents of eukaryotic cell membranes, which have important signalling roles in cells [1]. Disregulation of sphingolipid biosynthesis can therefore have dramatic effects on sphingolipid levels and result in disease states. As such, a detailed understanding of these enzymes, their enzymology and their structural biology is important to allow the rational design of enzyme specific inhibitors, which can be used to modulate sphingolipid biosynthesis and to allow us to understand how these enzymes are involved in disease.



The first enzyme on the biosynthetic pathway to sphingolipids is serine palmitoyl transferase (SPT), an integral membrane protein of the Endoplasmic Reticulum consisting of two subunits and a third small subunit [2]. We have constructed a fused SPT protein consisting of all three subunits which exhibits the same biochemical characteristics as the natural protein. Using this fused protein we have begun detailed biochemical and biophysical characterisation of the enzyme.

References:

1. A. H. Merrill. Chem. Rev., **2011**, 111, 6387-6422.
2. K. Gable, H. Slife, D. Bacikiva, E. Monaghan, T. M. Dunn, J. Biol. Chem., **2000**, 275, 7597-7603.

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ARTIFICIAL METALLOENZYMES FOR THE SELECTIVE FUNCTIONALIZATION OF HYDROCARBONS

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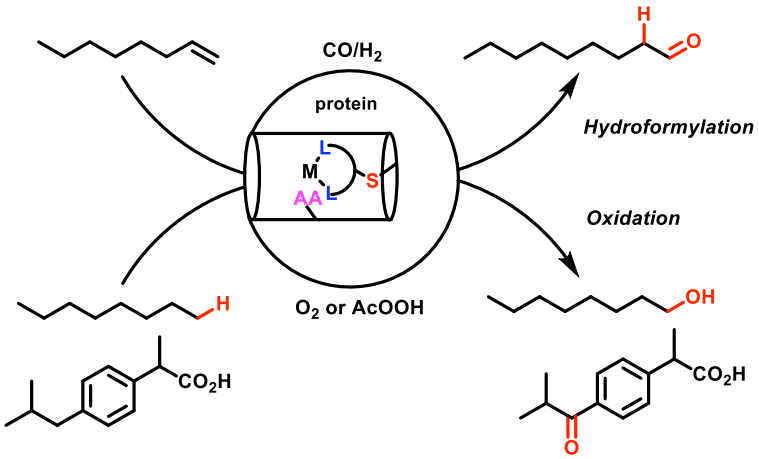
Author's Biography

I received my MChem from the University of St Andrews in 2007, before moving to the University of York to conduct my PhD on 'Multidentate phosphine-alkene ligands and their late-transition metal complexes' in the Fairlamb group. In 2011, I moved to France to carry out postdoctoral studies on nitrene transfer reactions in the Dauban group at the ICSN. In 2013, I moved back to St Andrews to work on artificial metalloenzymes in the Kamer group. In 2015, I obtained a Marie Curie Fellowship to work on 'ArtOxiZymes: Artificial Oxidation Enzymes for Highly Selective Waste Free Hydroxylation of Alkanes'. In October 2017, I will move to the University of Edinburgh to take up a Christina Miller Fellowship in the School of Chemistry.

Current Research Interest

One of the major challenges facing the chemical industries is the sustainable creation of chemicals from natural resources. Reactions such as the functionalization of C=C and C-H bonds lend themselves to sustainable processes, as they are atom economical. Increasing the selectivity of these reactions is an important goal to ensure these processes will be utilized by the chemical industries. Inspired by enzymes, which are highly selective catalysts, this work combines traditional homogenous catalysis and biocatalysis through the development of artificial metalloenzymes to create catalysts for the direct functionalization of hydrocarbon skeletons. Our focus is on increasing the linear selectivity of reactions such as the hydroxylation of n-alkanes and linear selective hydroformylation of long chain alkenes.



References:

1. A. G. Jarvis *et al*. *Angew. Chem., Int. Ed.* **2017**, Accepted.
2. M. V. Doble, A. C. C. Ward, P. J. Deuss, A. G. Jarvis , *Bioorg. Med. Chem.* **2014**, 22, 5657-5677.
3. P. J. Deuss, G. Popa, C. H. Botting, W. Laan, P. C. J. Kamer, *Angew. Chem., Int. Ed.* **2010,** 49, 5315-5317.

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Bacterial Imaging and Photodynamic Therapy (PDT) Using BODIPY-Polymyxin Conjugates

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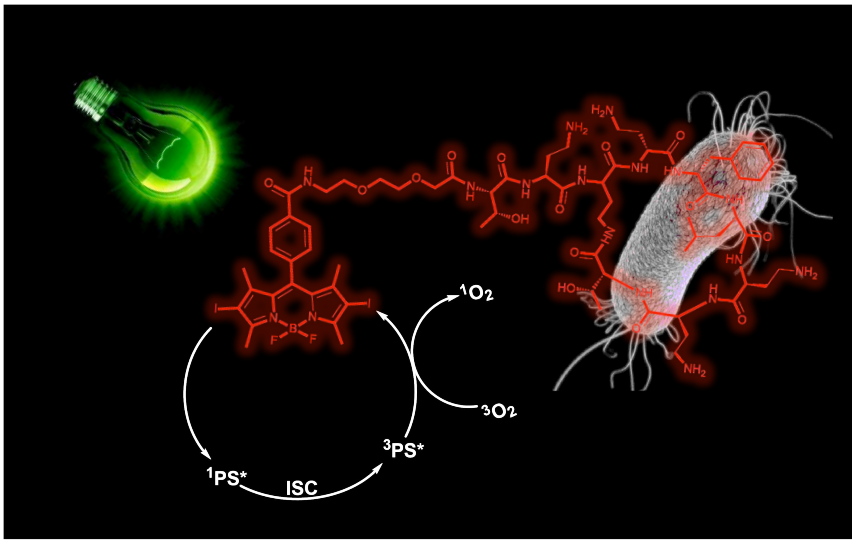
Author's Biography

Muhammed obtained his Bachelor of Science (2009) and Master of Science degrees (2011) in Chemistry from İzmir Institute of Technology (İztech). Then, he started his PhD research in the same department under the supervision of Assoc. Dr. Mustafa Emrullahoğlu. In May 2016 he received his PhD degree, studying on the design and synthesis of fluorescent molecules (BODIPY) for sensing and imaging applications. Muhammed joined Prof. Bradley's research group in November 2016 as a Postdoctoral Research Associate and is working in the synthesis of "smartprobes" for molecular imaging and development of analytical assays for "GMP" analysis.

Current Research Interest

Increasingly bacteria are developing resistance to the current arsenal of antimicrobial agents and there is thus is an urgent need to develop selective and sensitive methods for bacterial infections. Photodynamic therapy (PDT) is widely utilised for chemotherapy of surface tumors, and utilizes a photosensitizer that is activated with visible light and produces highly toxic singlet-oxygen from its triplet form.

In this study, we have developed BODIPY-based probes that selectively bind bacteria and allow their fluorescent detection, with the penta-cationic war-head polymyxin used as targeting unit. Here bis-iodo-Bodipy-polymyxin (**I_2-BOD-PMX**) was developed as a method of binding and killing bacteria.



References:

1. M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* **2002**, 233, 351–371.
2. M. R. Hamblin, *Curr. Opin. Microbiol.* **2016**, 33, 67–73.
3. A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, *Chem. Soc. Rev*. **2013**, 42, 77–88.
4. D. R. Rice, H. Gan, B. D. Smith, *Photochem. Photobiol. Sci*. **2015**, 14, 1271–1281.

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LIVING GENOCHEMETICS: SYNCHRONOUS BIO-HALOGENATION AND CATALYTIC CROSS-COUPLING IN BACTERIAL CULTURES

Author: Sunil V. Sharma, Cristina Pubill-Ulldemolins, Xiaoxue Tong, Christopher Cartmell, Enrico Marelli, Refaat Hamed & Rebecca J. M. Goss*

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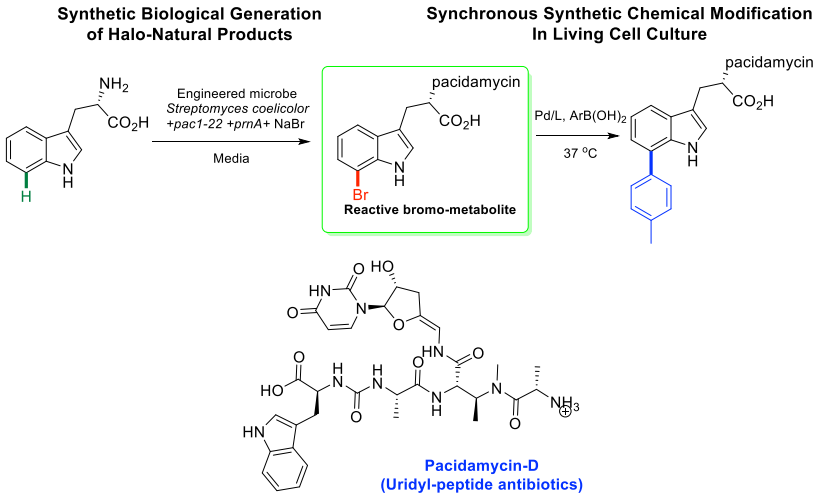
Author's Biography (approx. 50–100 words)

With a background in Pharmceutical technology/chemistry (M. Pharm, 1996, India) and PhD in synthetic chemistry (Dr S. Bew, University of East Anglia, Norwich, 2008), I developed keen interests in the synthesis of bioactive molecules, total synthesis of natural products and developing analytical tools for biochemical processes. After a post-doc (with Dr C. Hamilton, 2010, UEA, Norwich), I joined as a research fellow in the multi-disciplinary projects with Dr R. J. M. Goss (St Andrews, 2014).

Current Research Interest (approx. 200–300 words + scheme)

Bacterial natural products (NP) represent an unparalleled starting point for drug discovery, and NP analogues are desired to study modes of action, determine SAR and improve bioavailability/ bioactivity. However, the generation of NP analogues is often very challenging. Combining synthetic biology with synthetic chemistry provides a powerful approach toward NP diversification, utilizing the expediency and synthetic capability of biosynthetic pathways and chemical diversity enabled by organic synthesis. **Genochemetics** is new approach pioneered by Goss group to facilitate NP analogue generation, where genetic modification is used to install an orthogonal handle into a complex NP scaffold that enables site-selective synthetic diversification, without employing protecting group chemistry. We envisaged that by installing a sufficiently reactive handle (e.g. a C-Br bond) and developing compatible mild aqueous chemistries, synchronous biosynthesis of the tagged metabolite and its subsequent chemical modification in living culture can be achieved.[1]



References:

1. S. V. Sharma, X. Tong, C. Pubill-Ulldemolins, C. Cartmell, E. J.A. Bogosyan, E. J. Rackham, E. Marelli, R. B. Hamed & R. J.M. Goss, *Nature Commun.* **2017, in press.**

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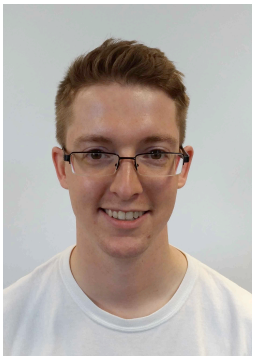
Mechanistic Studies into Rhodium Catalysed Silylation Reactions



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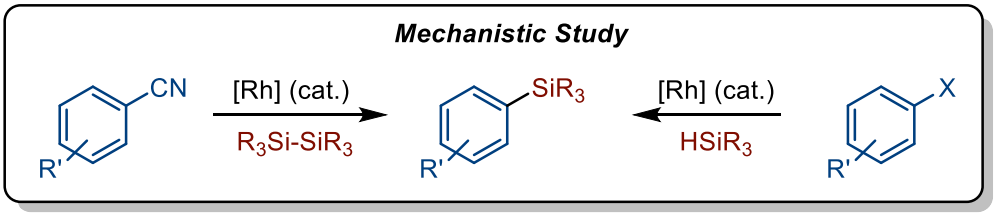
Author's Biography (approx. 50–100 words)

Eric completed his BSc. degree at the University of Western Ontario in 2009, completing his fourth year project with Professor Elizabeth Gillies. He completed his Ph.D. at Queen's University under the supervision of Professor Cathleen Crudden on the synthesis of transition and main group metal N-Heterocyclic and Mesoionic Carbenes complexes, and their catalytic applications. In 2015, Eric undertook an NSERC funded post-doctoral fellowship at the University of Edinburgh working with Professor Guy C. Lloyd-Jones FRS.

Current Research Interest

Aryl silanes are highly versatile synthetic intermediates which undergo a wide variety of synthetic transformations.[1] These reagents are typically synthesized utilising highly reactive aryl lithium reagents which are not compatible with a wide variety of functional groups. The transition metal catalysed cross coupling of aryl electrophiles with silanes, or disilanes presents a more atom-economical approach. Unfortunately, these transformations are plagued with problems such as poor substrate compatibility, low yields, high temperatures and catalyst loadings, and byproduct formation.[2] In part, these limitations stem from poor mechanistic understanding of these transformations which have been largely unexplored. This work describes our mechanistic studies on rhodium catalysed silylation reactions of aryl electrophiles using air and moisture stable silane derivatives. To accomplish this task, we have taken advantage of in situ analysis using NMR spectroscopy to study kinetics and observe highly reactive intermediates.[3]



Detailed Kinetic Analysis
Isotopic Labelling/Intermediate Detection
In situ analysis using ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR.

References:
1. Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011,** 40, 4893-4901
2. Y. Yamanoi, H. Nishihara, *J. Org. Chem.* **2008,** 73, 6671-6678
3. E. C. Keske, G. C. Lloyd-Jones, *Unpublished Results*

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SAPO STA-20: A Novel Zeotype prepared by Co-Templating Methods

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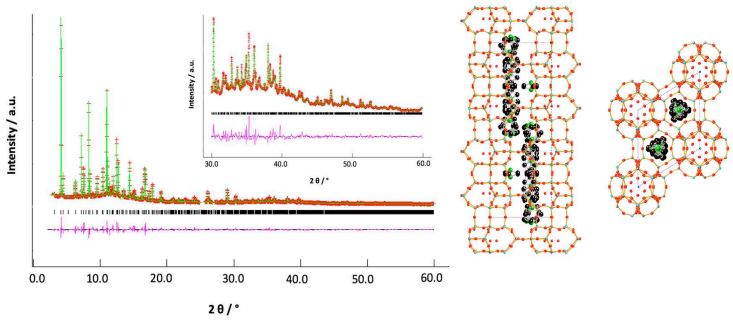
Author's Biography

After graduating from Cardiff University with a Masters in Chemistry/ MChem (first class honours) in July 2015, I started in my PhD studies at University of St Andrews in September 2015 under the supervision of Prof Paul Wright.

Current Research Interest

My current research interests involves the use of templating to prepare new zeolitic catalysts, an example of which is given below.

The synthesis of the novel silicoaluminophosphate, STA-20, has been achieved using the organic structure directing agents hexamethylene bisdiazabicyclooctane (diDABCO-C6) and trimethylamine (TrMA) in a co-templating strategy.[1] This co-templating approach was first reported by Turrina *et al*. in the synthesis of SAPO-56 (AFX) and novel SAPOs STA-18 (SFW) and STA-19(GME).[2] STA-20 belongs to the ABC-6 family of structures and has a small pore system which type has been shown to have potential in catalytic applications, e.g. STA-7 & STA-14 in MTO reactions.[3] Here we describe details of the synthesis, structural refinement for calcined STA-20 and how its structure has been solved using a multi-technique approach including molecular modelling and diffraction methods.



Rietveld refinement for as-prepared, dehydrated STA-20. Space group P- 31c, a = 13.17406(12) Å, c = 30.0910(9) Å, R_{wp} = 5.70 %.

Acknowledgements: This work has been supported by Johnson Matthey PLC, UK. We acknowledge Diamond Light Source for time on beamline I11 under Proposal EE11830-1.

References:

1. A. Turrina, R. Garcia, A. E. Watts, H. F. Greer, J. Bradley, W. Zhou, P. A. Cox, M. D. Shannon, A. Mayoral, J. L. Casci and P. A. Wright, *Chem. Mater.*, 2017, **29**, 2180–2190.
2. A. Turrina, R. Garcia, P. A. Cox, J. L. Casci and P. A. Wright, *Chem. Mater.*, 2016, **28**, 4998–5012.
3. M. Castro, S. J. Warrender, P. A. Wright, D. C. Apperley, Y. Belmabkhout, G. Pirngruber, H.-K. Min, M. B. Park and S. B. Hong, *J. Phys. Chem. C*, 2009, **113**, 15731–15741.

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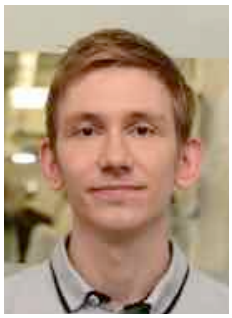
^{13}C-TMS-diazomethane – a versatile reagent for labelling studies



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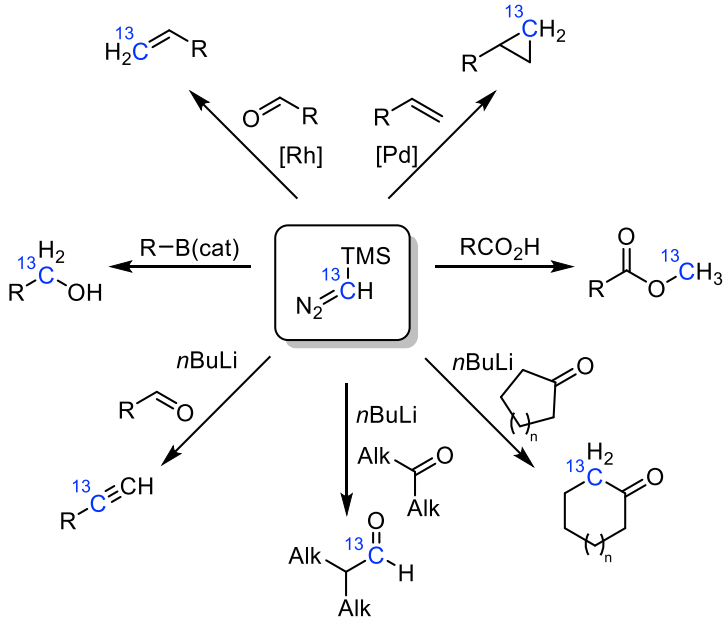
Author's Biography

Chris obtained his B.Sc. in Ireland at the Galway-Mayo Institute of Technology. He later completed his Ph.D. at University College Dublin in 2016 for the design of novel ligands and catalysts for asymmetric synthesis under the supervision of Prof. Pat Guiry. After a short post-doctoral stay in the same group, Chris moved to Edinburgh to join the group of Prof. Guy Lloyd-Jones FRS as an ERC funded post-doctoral researcher in late 2016.

Current Research Interest

Trimethylsilyl diazomethane (TMSDAM) is an incredibly versatile reagent for organic synthesis.[1,2] Under basic conditions, it behaves as a nucleophile, while under acidic conditions it becomes an electrophile. Under neutral conditions it can act as a C-N-N synthon in 1,3-dipolar cycloadditions or as a C-1 unit in carbenoid chemistry such as cyclopropanations and alkenylidene reactions. However, despite over 10,000 recorded uses on Reaxys®, to date there exists no preparation of a ^{13}C-labelled TMSDAM isotopologue. As this compound would be highly valuable for labelling studies, we have developed a high-yielding, chromatography free synthesis of ^{13}C-labelled TMSDAM starting from ^{13}C-MeOH.[3] We aim to demonstrate the utility of this reagent through the preparation of various ^{13}C-labelled intermediates and products.



References:

1. J. Podlech, *J. Prakt. Chem.* **1998**, 340, 679-682
2. T. Shioiri, T. Aoyama, *J. Synth. Org. Chem. Jpn.* **1996,** 54, 918-928
3. C. Nottingham, G. Lloyd-Jones, manuscript in preparation

University of St Andrews

EaStCHEM
The Edinburgh and St Andrews Research School of Chemistry

EaStCHEM Conference for Early-Career Researchers 2017

Expanding the GenoChemetics toolkit with new aqueous cross coupling methodologies

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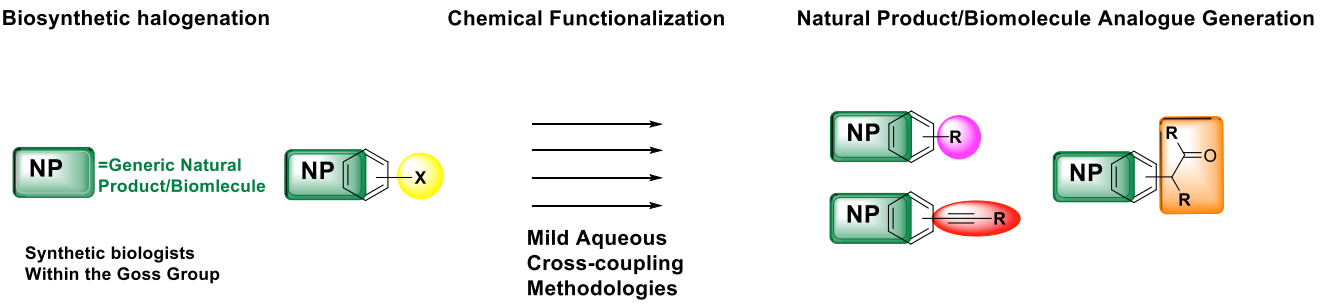
I am an organic/computational chemist with a focus on the biosynthesis and synthetic modification of biomolecules. Starting from an MSc in catalysis, my PhD transcended organometallic and computational chemistry (ICIQ and URV, Spain). In addition, I gained expertise in synthesis of bioactive compounds during a postdoctoral tenure at the ITbM, Japan. Strategically, I next joined the multidisciplinary Goss group as a Marie Curie postdoctoral fellow to learn about reprogramming biosynthesis while developing mild-aqueous methods for new to nature bio-metabolite functionalisation.

Natural Products (NPs) are key to medicine, however the generation of analogues of these important compounds can often be challenging. In this context, palladium cross-coupling reactions are a powerful tool in synthesis and potentially for late-stage derivatisation of NPs. Building upon a previous successful approach pioneered by our group,[1] we have developed methodologies to enable, under mild aqueous conditions, a greater diversity of cross-coupling reactions of aryl halide containing small molecules, amino acids and peptides or structurally complex NPs.[2-3]



References:

1. A. D. Roy, S. Grüschow, N. Cairns, R. J. M. Goss, *J. Am. Chem. Soc.*, **2010**, 134, 1224-12245
2. M. J. Corr, S. V. Sharma, C. Pubill-Ulldemolins, R. T. Bown, P. Poirot, D. R. M. Smith, C. Cartmell, A. Abou-Fayad, R. J. M. Goss, *Chem. Sci.*, **2017**, 8, 2039-2046
3. E. Marelli, Y. Renault, S. V. Sharma, S. P. Nolan, R. J. M. Goss, *Chem. Eur. J.*, **2017**, 23, 3832-3836

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URANYL REDUCTION IN A REDOX-ACTIVE LIGAND

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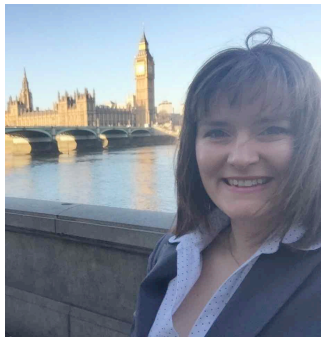


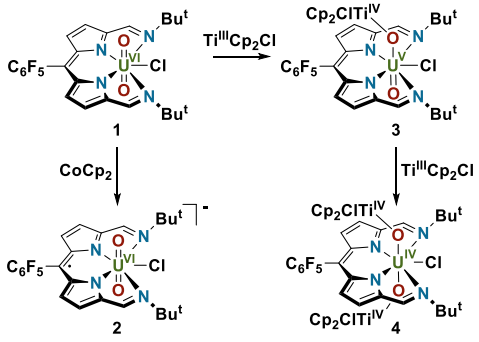
Author's Biography

After graduating from Heriot-Watt university in 2008, I worked in industry for a year before undertaking my PhD at the University of Edinburgh with Dr Phil Bailey on the synthesis of asymmetric ligands. During my PhD I won a Teaching in Higher Education scholarship which gave me experience in tutoring and lecturing. Whilst writing my thesis in 2012 I developed a research proposal to study actinide carbene bonding with Prof. Polly Arnold and was awarded a Doctoral Prize Fellowship for two years. I am now the senior postdoc in the Love/Arnold group and work on developing novel complexes containing actinide ligand multiple bonds. In 2017 I was selected for the Sci-Finder future leaders program from an international field.

Current Research Interest

Redox-active ligands can provide alternative redox pathways in metal complex chemistry that are not available using "innocent" ancillary ligands. While these features have been studied extensively in TM complexes, the use of redox-active ligands in actinide chemistry is less developed. This is surprising, as significant advances have been made in the reduction chemistry of the uranyl dication, a reaction important to uranium remediation, *e.g.* forming stable, oxo-functionalised uranyl(V) compounds and reduction of uranyl(VI) β-ketoiminate complexes to U(IV) facilitated by oxo-coordination of boron Lewis acids.

We recently reported the straightforward synthesis of the mono-anionic, tetradentate dipyrrin ligand, $L^{-\cdot}$. Here, we will demonstrate how it allows access to new, ligand-mediated, uranyl reduction chemistry: we report a uranyl(VI) complex of L^{-} and its contrasting inner- and outer-sphere redox chemistry, both of which routes involve the redox-active dipyrrin.[1]



Scheme 1: Reduction of uranyl dipyrrin complexes by inner- and outer-sphere mechanisms.

The expanded Schiff-base dipyrrin is a non-innocent partner in uranyl reduction. Reduction of **1** by the outer-sphere reductant $CoCp_2$ yields a U(VI) ligand radical anion **2** whilst reduction with an inner-sphere Ti(III) reagent yields the doubly titanated U(IV) product **4**. The redox non-innocent ligand is key to both reduction pathways, with DFT and spectroscopic evidence showing that the first step in both reactions involves a ligand based reduction. Isolation of the U(IV) complex **4** from reaction with the relatively mild reductant Ti(III) further reinforces the understanding that oxo-coordination of the uranyl to the Lewis-acidic Ti(IV) metallocene renders the complex more susceptible to reduction and fits well with previous results on the use of other Lewis acids to mediate $[UO_2]^{2+}$ reduction chemistry.

References:

1. J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S. Sproules, P. L. Arnold and J. B. Love, *Chem. Sci.*, 2017, **8**, 108-116.

EaStCHEM Conference for Early-Career Researchers 2017
University of St Andrews
Thursday 7th September 2017

0930–1000 **Registration, Welcome Coffee and Poster Hanging**

1000–1110 Session 1 – Academic Keynote Address (Physics Theatre A)

1000–1010 Welcome and Opening Remarks
Prof. David O'Hagan

1010–1100 **KEYNOTE SPEAKER –** Dr Alyssa-Jennifer Avestro *(Durham University)*
Life in the Fast Lane: Catalysing an independent career & making it all count

1100–1110 **Comfort Break**

1110–1210	**Session 2 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Eoin Gould*	Physics Theatre C *Chair: David McKay*
1110–1125	Photoaffinity labelling identifies the target of trypanocidal bis-tetrahydropyran 1,4-triazoles **Lindsay B. Tulloch**	Pump-probe simulation of CS_2 and CHD: time-dependent photoionization **Maria Tudorovskaya**
1125–1140	Serine palmitoyltransferase protein interaction landscape and structural characterisation **Van Kelly**	Ador synthesis realized by use of the hydrostatic pressure **Michal Mazur**
1140–1155	Imaging intracellular drug distribution using stimulated raman scattering microscopy **William J. Tipping**	Manipulation of polar order in ferroelectric 'Empty' tetragonal tungsten bronzes **Jonathan Gardner**
1155–1210	Ensemble based drug design: a new paradigm in drug discovery **Jordi Juárez-Jiménez**	Synthesis of magnetic polyhedral: cubes and triangular bipyramids **Sergio Sanz**

1210–1340 Lunch, Exhibition and Poster Session (School of Physics Common Space)

1340–1440	**Session 3 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Tamara Kosikova*	Physics Theatre C *Chair: Amanda Jarvis*
1340–1355	Mechanistic studies on nucleophilic trifluoromethylation of carbonyls with the Ruppert-Prakash reagent **Thomas West**	Structure and reactivity of Cu-doped Au(111) surfaces **Federico Grillo**
1355–1410	Aryloxide-facilitated catalyst turnover in α,β-unstaurated acyl ammonium catalysis **Mark D. Greenhalgh**	Development of peptide-based electrochemical sensors **Eva González-Fernández**
1410–1425	Studying the mechanism of C–O cleavage in lignin model compounds by ruthenium-xantphos catalysis **Rebecca C. How**	*In-situ* thermal battery discharge using NiS_2 as a cathode material **Julia Payne**
1425–1440	Towards the rational design of isoform-selective cyclophilin ligands **Alessio De Simone**	Whither crystallography… A view from the ground **David B. Cordes**

1440–1510 Afternoon Coffee (School of Physics Common Space)

1510–1540	**Session 4 – Early Career Researcher Presentations**	
	Physics Theatre A *Chair: Mark Greenhalgh*	Physics Theatre C *Chair: Rebecca How*
1510–1525	Single-molecule transmembrane supramolecular chemistry **Stefan Borsley**	Molecular magnets under pressure **Helen Duncan**
1525–1540	Capsules for molecular recognition and catalysis **Vicente Marti-Centelles**	Difference in reactivity of two zinc binding plant metallothioneins isoforms **Hasan Tanvir Imam**

1540–1550 **Comfort Break**

1550–1650 Session 5 – Industry Keynote Address (Physics Theatre A)

1550–1640 **KEYNOTE SPEAKER –** Dr Nathaniel Cain *(Afton Chemical)*
An Engineer's Career Path to Chemistry and Exploiting the Interface

1640–1650 Concluding Remarks and Prizegiving (Physics Theatre A)
Neil Keddie and Amanda Jarvis

1650–1800 Wine Reception (School of Physics Common Space)

[END]