67th Irish Universities Chemistry Research Colloquium

Maynooth University 2015

25th-26th June 2015

Department of Chemistry, Maynooth University

BOOK OF ABSTRACTS

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Conference Website

https://www.maynoothuniversity.ie/chemistry/chemistry-colloquium-2015

67th Irish Universities Chemistry Research Colloquium

Maynooth University 2015

Sponsors

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General Information:

The 67th Irish Universities Chemistry Research Colloquium will take place on Thursday 25th June and Friday 26th of June, 2015. Should you have any queries during the Colloquium, which are not answered below, please contact one of the Colloquium organisers at our information desk or call the departmental office on 01-7083770. The information desk will be manned in the foyer of the John Hume Building (JHB), see map, during the coffee breaks.

Registration:

Registration will take place in the JHB on Thursday 25th of June from **8.45 am**. Each delegate will receive a welcome pack on registration. Speakers should present themselves to the Colloquium organisers at the registration desk. Delegates presenting posters should mount their display on the poster boards in the Phoenix restaurant (upstairs), see map, on the morning of Thursday 25th of June from **8.45 am**.

Oral Presentation Sessions:

The oral presentations will be held in parallel sessions in Lecture Theatres 2 and 3, located on the ground floor of the JHB. Please arrive early so as not to disturb the speakers. A separate practice room will be available all day on Thursday and Friday in Lecture Theatre 4. If you wish to avail of this facility please contact the information desk.

Poster Session:

There are two poster sessions on Thursday 25th of June during which delegates are encouraged to view posters that will be on display. The first poster session will take place at **15.55 pm** in the Phoenix restaurant (upstairs), see map. Tea and coffee will also be served. The second poster session will take place at **17.50 pm** in the same location. This session will include a wine and cheese reception. Tickets for the wine and cheese reception can be found in your welcome pack.

Coffee Breaks:

There are coffee breaks both mornings of the Colloquium, at **11.00 am** on Thursday and **11.15 am** on Friday. The coffee breaks will take place in the foyer of the JHB.

Lunch:

There are several cafes and restaurants in Maynooth town where delegates may wish to have lunch.

Colloquium Barbeque:

The Colloquium barbeque will take place in Pugin Hall on the south campus, see map, on the Thursday evening. The welcome pack contains your barbeque tickets, which must be presented to gain access to this event. Delegates are asked to be in Pugin Hall by **8.00 pm**.

Banking and Parking:

There is an ATM at the northern entrance to the Science Building, the entrance facing the JHB. Parking is available on campus free of charge (parking permits are not required). Car Park 9 is the recommended carpark.

Internet Facilities:

Wireless Instructions for Mac OS X

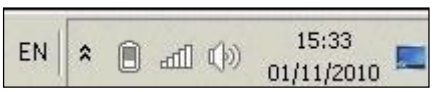
Ensure that the wireless radio is turned on by clicking on the Airport icon and then choosing "turn Airport on"

Click on the Airport icon and click CONF, there will be a checkbox beside CONF if you are already connected.

The required password will be **welcome-2-mu-475665**.

Windows 7 Wireless Connection Instructions:

Click on the wireless icon on the bottom right tool bar.



You can then view which networks are available to you.

Choose CONF and select the connect button.

Enter the password **welcome-2-mu-475665** to connect.

Note: If you have connected to conf in the past it might be best to delete or forget the old wireless profile and re-connect.

Award Ceremony and Closing Address:

The award ceremony and closing address will be held in Lecture Theatre 2 in the JHB on Friday 26th of June at **12.35 pm**. Delegates should attend and any presenters who are unavailable to attend should nominate a person to collect a prize in their absence.

Social Activities:

In addition to the Colloquium barbeque, there is Ghost Tour at **18.45 pm** which will leave after the evening poster session. Maynooth University has a very historic and interesting campus so it is well worth taking the tour to find out more! The tour will end at the National Science and Ecclesiology Museum which is located on the south campus, see map. The museum will open especially for your perusal. After the barbeque delegates are invited to enjoy an evening of music in Brady's pub located on the main square of Maynooth.

Thursday 25th June

8:45	**Registration**	
	JH2 Lecture Theatre	
9:30	Welcome and Opening remarks	
	Opening Session	
9:45	**Keynote Lecture: *Prof. A.P. Davis,* (University of Bristol)** *Synthetic Lectins - Biomimetic Receptors for Carbohydrates*	
10:35	**T. McGivern (RCSI)** *Multifunctional Cu drug candidates as potential innovative anti-cancer agents*	
11:00	***Coffee Break***	
	JH2 Lecture Theatre	***JH3 Lecture Theatre***
	Session A1	**Session B1**
11:20	**C. Nottingham (UCD)** *Ferrocene-based Ligands for Asymmetric Catalysis*	**J. Bugler (NUIG)** *Combustion chemistry: Do we even understand how alkanes burn?*
11:45	**J. O'Sullivan (MU)** *Pyrene Functionalised Calixarenes as Metal Sensors*	**N. Abdallah (UL)** *Sequential immobilization of catalysts for application in cascade reactions*
12:05	**S. Bradberry (TCD)** *Self-Assembly for Luminescence: Ln(III)-coordination chemistry in generation of sensors and soft-materials*	**S. Dick (QUB)** *Detection of Single Base Substitutions in 25-mer Oligonucleotides Using Surface-enhanced Raman Spectroscopy*
	Flash Presentations	***Flash Presentations***
12:30	**C. O'Connor (UCD)** *Ruthenium β-Diketiminate Complexes as Catalysts for the Rapid and Efficient Dehydrogenation of Amine Boranes*	**I. Meazzini (TCD)** *Targeted β-phase formation in poly(fluorene)-ureasil grafted organic-inorganic hybrids*

	S. McMahon (DCU) *The use of Fluorescent BODIPY Metal Carbonyls to Function as CO Releasing Molecules*	**C. McCrellis (QUB)** *Effect of the Presence of MEA on the CO_2 Capture of Superbase Ionic Liquids*
	F. Mutuma (DIT) *Novel Magnetic reservoirs for targeted drug delivery*	**G. Flynn (UL)** *Growth of tin seeded multi-segment silicon-germanium axial heterostructure nanowires in a wet chemical solvent vapour growth system*
12:50	***Lunch***	
	Session A2	**Session B2**
14:40	**Academic Lecture:** **Dr. R. Evans, (TCD)** *Novel approaches to luminescent solar concentrator design using organic-inorganic hybrid waveguides*	**Academic Lecture:** **Prof. D. Diamond, (DCU)** *Bio-Inspired Active Fluidic Systems based on Stimuli-Responsive Materials*
15:05	**K. Barton (DIT)** *Hydrogen Bonding and its Effect on Alkoxysilane Condensation*	**G. Duffy (UCC)** *Development of chemically modified screen printed carbon electrodes for caffeine and mouse IgG detection*
15:30	**J. Vasconcelos (TCD)** *Investigation of phospholipid conditioning of carbon surfaces for applications in biomaterials*	**M. Doran (MU)** *Development of a Biosensor for the Real Time Neurochemical Monitoring of Superoxide*
15:55	***Coffee Break and Poster Session***	
	Session A3	**Session B3**
16:40	**R. Fagan (DIT)** *Improved High Temperature Stability of Anatase TiO_2 Photocatalysts*	**T. O'Hara (ITT)** *TOXOR: Design and Application of an Electrochemical Toxicity Biosensor for Environmental Monitoring*
17:05	**T. Flannelly (UL)** *Mechanism and Kinetics of Advantaged Biofuels Synthesis from D-Fructose*	**S. O'Callaghan (UCC)** *Implantable pH sensors for monitoring of oral health in the elderly*

	Flash Presentations	***Flash Presentations***
17:30	**M. Ahmed (MU)** *Derivatised Phens: The Quest for New Anti-Tuberculosis Drugs*	**E. Giraud (UCC)** *Vapour phase methods for inclusion of inorganic materials into block copolymer patterns*
	D. Keogan (RCSI) *Bismuth Hydroxamic Acid Complexes as Potential anti-H. pylori Agents*	**N. Kamali (NUIG)** *Polymorphism in two Model Active Pharmaceutical Ingredients*
17:50	***Wine and Cheese Poster Session***	
18:45	***Ghost Tour and Science museum***	
19:15	*Break*	
20:00	***BBQ at Pugin Hall***	

Friday 26th June

	JH2 Lecture Theatre	***JH3 Lecture Theatre***
	Session A4	**Session B4**
10:00	**H. Prydderch (DCU)** *Imidazolium and Pyridinium Ionic Liquids from Mandelic Acid; Synthesis, Biodegradation and Toxicity Evaluation*	**S. Shannon (UCD)** *Nano-Assembly of Molecular Spin Switches*
10:25	**S. Soldatou (NUIG)** *Marine organisms as a source of bioactive metabolites*	**C. Tumilson (QUB)** *Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for In-Situ Analysis of Co-Electrolysis*
10:50	**H. Daly (RCSI)** *Off to On Switching Cellular Uptake Responsive NIR Fluorescent Nanoparticles*	**W. Francis (DCU)** *Chemotactic and Electrotactic Self-Propelled Ionic Liquid Droplets*
11:15	***Coffee Break***	
11:45	**Keynote closing lecture: *Dr. M. McCann***, *Maynooth University*	
12:35	Awards and concluding remarks	

Opening Session
JH2
9.30 am – 11.00 am

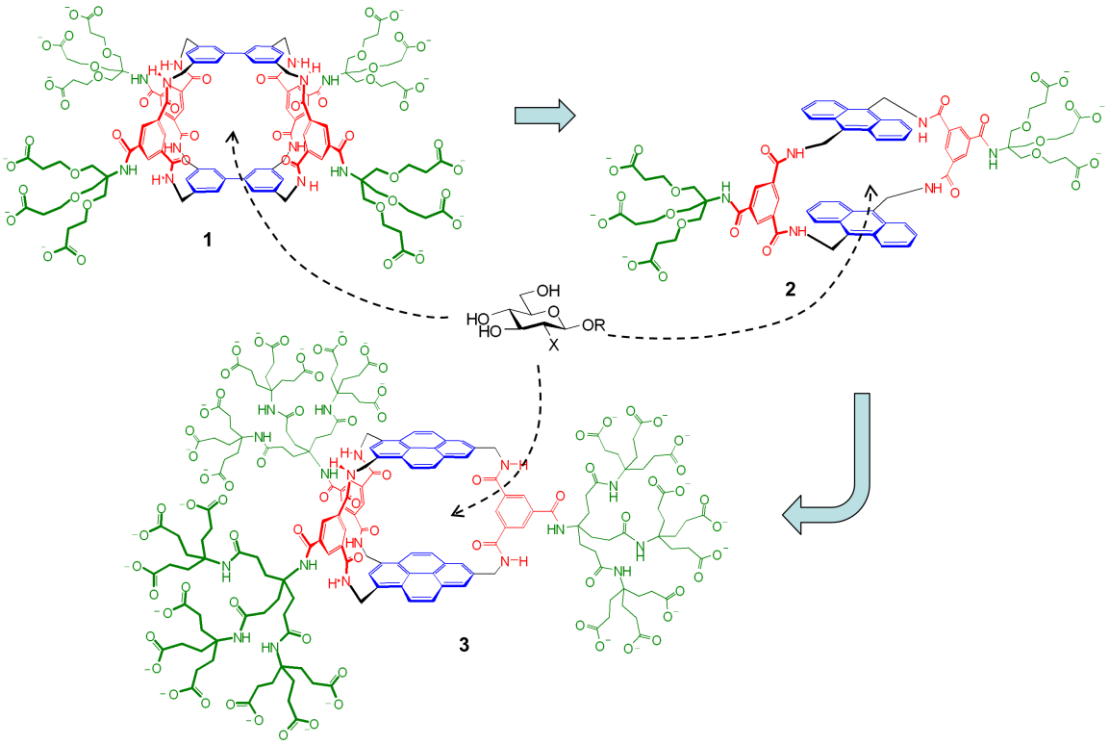
Keynote Lecture

Synthetic Lectins - Biomimetic Receptors for Carbohydrates

Anthony P. Davis
School of Chemistry, University of Bristol

Abstract:

Carbohydrate recognition presents an interesting problem to supramolecular chemists. On the one hand it is challenging, owing to the hydrophilic and hydromimetic nature of carbohydrates. Indeed, even natural lectins tend to show low affinities by normal biological standards. On the other hand, it provides an opportunity to interface directly with biology. Lectins are widely used as tools in glycobiology, but do not always possess the ideal recognition and/or physical properties. "Synthetic lectins" could serve as complementary agents if sufficiently active and selective. We have been developing receptors for the "all-equatorial" family of carbohydrates (glucose, GlcNAc etc.), employing designs which incorporate parallel aromatic surfaces (complementary to axial CH units) joined by polar spacers. As illustrated below, the systems have evolved from biphenyl-based structures (e.g. **1**) through monocyclic bis-anthracenes (e.g. **2**) to cages built from condensed aromatics (e.g. **3**). This diversity of structures has lead to useful variations in selectivity, while affinities continue to improve. Some of this new work has led to systems with affinities > 10^4 M^{-1} towards saccharides in water, providing a serious challenge to common natural lectins.



Email: anthony.davis@bristol.ac.uk

Oral Presentation

Multifunctional Cu drug candidates as potential innovative anti-cancer agents.

Mc Givern, T.J.P[a*]; Kellett, A[b] & Marmion, C.J[a].

[a]Centre for Synthesis and Chemical Biology, Department of Pharmaceutical and Medicinal Chemistry, Royal College of Surgeons in Ireland, 123 St. Stephen's Green, Dublin 2 and [b]School of Chemical Sciences and National Institute for Cellular Biotechnology, Dublin City University, Glasnevin, Dublin 9.

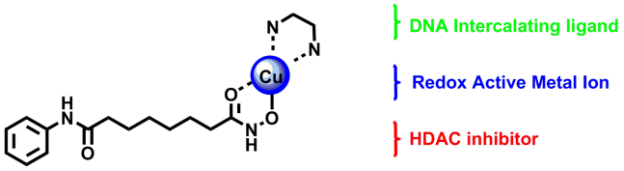


Figure 1 Multifunctional Cu drug candidates

Abstract:

The development of oxidative chemical nuclease agents remains a focal point of modern medicinal inorganic chemistry, owing to the redox properties of some *d* block transition metal elements - Cu for instance. Recent progress has shown that compounds of this class possess enhanced cytotoxicity activity, and *in vivo* cytotoxic tolerance[1]. Owing to the DNA binding and scission capabilities of Cu^{II} complexes[2] this has significantly contributed towards metallodrug design and action. Similiarly, the design, synthesis and evaluation of enzyme inhibitors rationally chosen for their potential in suppressing tumour cell proliferation has also been a major goal, one such example being histone deacetylase (HDAC) enzymes. The clinically approved HDAC inhibitor suberoylanilide hydroxamic acid (SAHA) has potent anti-cancer activity. It has also been shown to have selectivity towards tumour cells over normal cells. To date, we have successfully synthesized a library of novel Cu-SAHA complexes bearing various designer DNA intercalating ligands, (Figure 1). Compared with the well-studied chemical nuclease $[Cu(Phen)_2]^{2+}$, these complexes have considerable *in vitro* cytotoxic activity, enhanced DNA binding properties and efficient chemical nuclease activities. Our recent results suggest that these complexes warrant further pharmacological evaluation. Ultimately our goal is to generate a new class of chemotherapeutic with dual HDAC inhibitory and chemical nuclease activity, as such, a summary of our results to date will be presented.

References:

1 (*a*) A. Prisecaru; A. Kellett *et al.*, *Chem. Comm.* **2012**, *48*, 6906. (*b*) M. McCann; A. Kellett *et al.*, *Chem. Comm.* **2013**, *49*, 2341.

2 (*a*) A. Prisecaru; A. Kellett *et al.*, *J. Med. Chem.* **2013**, *56*, 8599. (*b*) Z. Molphy; A. Kellett *et al.*, *Inorg. Chem.* **2014**, *53*, 5392.

Email: tmcgivern@rcsi.ie

Session A1
JH2
11.20 am – 1.00 pm

Oral Presentations

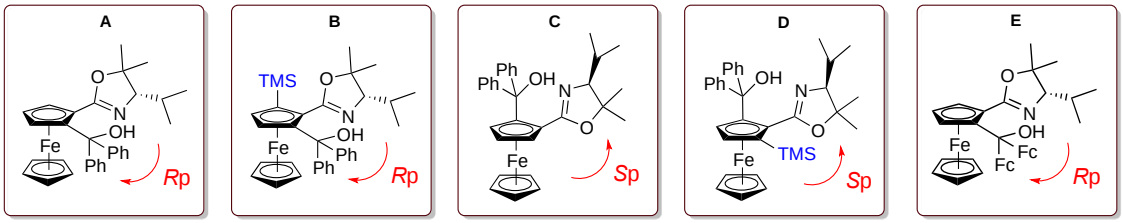
Ferrocene-based Ligands for Asymmetric Catalysis

Nottingham, C.* and Guiry. P.J.
Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

Abstract:

The preparation of enantiopure compounds is an indispensible area of research in modern chemistry. To this end, the use of readily modifiable chiral donor ligands coupled with metal catalysts has emerged as one of the most popular strategies for asymmetric synthesis.[1] However, effective chiral ligands are generally quite expensive and in many cases this serverly limits their application.

Herein we present the synthesis and application of a range of novel ferrocene-oxazoline *N*,*O* ligands bearing both central and planar chirality (Ligands **A - E**). These ligands are designed to exploit the *gem*-dimethyl effect in order to mimic the performance of more expensive ligands but at a fraction of the cost.[2] In order to test our ligands we have applied them in the enantioselective diethylzinc addition to aldehydes as a model reaction, followed by the more challenging phenylzinc addition to aldehydes.[3,4]



FeOx (R_p) $Ph_2C(OH)$ | FeOx (R_p) $Ph_2C(OH)$ (R_p) TMS | FeOx (S_p) $Ph_2C(OH)$ | FeOx (S_p) $Ph_2C(OH)$ (S_p) TMS | FeOx (*Rp*) $Fc_2C(OH)$ Fc = Ferrocene

Following on from this work we have designed and synthesised a new, ferrocene-based chiral ligand scaffold. This scaffold is synthesised from cheap and readily available starting materials in enantiopure form utilizing only a catalytic amount of chiral input. The transformation of this scaffold into a series of mono- and bidentate ligands for use in asymmetric catalysis is underway and some preliminary results will be presented.

References:

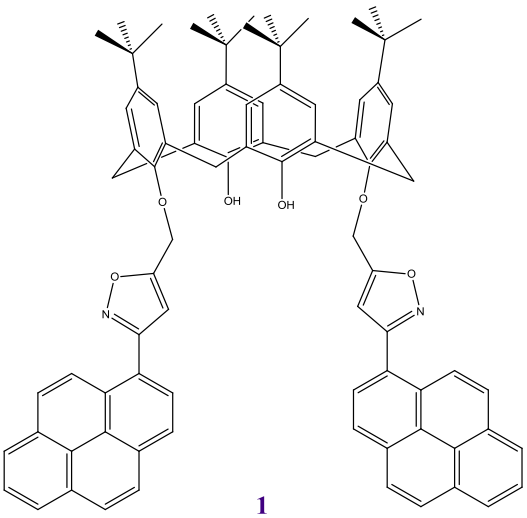
[1] Pfaltz, A.; Drury, W. J. *Proc. Natl. Acad. Sci. U. S. A.*, **2004**, *101*, 5723.
[2] Paquin, J. F; Belanger, E.; Pouliot, M.; *Org. Lett.*, **2009**, 11, 2201.
[3] Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823.
[4] Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444.

Email: p.guiry@ucd.ie

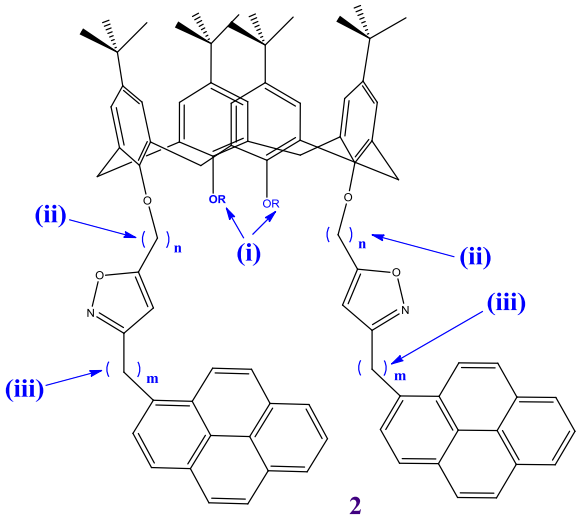
IRISH RESEARCH COUNCIL
An Chomhairle um Thaighde in Éirinn

Pyrene Functionalised Calixarenes as Metal Sensors

O'Sullivan, J.*; Twamley, B., Heaney, F.
Department of Chemistry, Maynooth University, Maynooth, Co. Kildare.



1
PIC
Pyrene Isoxazole Calixarene



2
R ≠ H, n ≠ 1, m > 0

Abstract:

Functional calix[4]arenes are well recognised sensors of both cationic[1] and anionic[2] species. Recent work in our laboratory has established the potential of **PIC,** the pyrene-isoxazole calixarene, **1**, as a selective detector of Cu^{2+} ions in the presence of a range of other metal cations.[3, 4] This paper will discuss progress towards a determination of the mode of complexation between the copper ions and the host molecule. In particular the roles of the calix[4]arene core and the pendant arms will be discussed by reference to analogues of **PIC** which have been designed to establish the relative importance of each of the following for engagement between the host and the metal ion: (i) the lower rim hydroxyl groups, (ii) the length of spacer between the calix[4]arene core and the isoxazole moieties and (iii) the length of spacer between the pyrene and the heterocyclic moieties. This paper will report on the design, synthesis, and ion binding characterisation of the novel calixarenes, **2**.

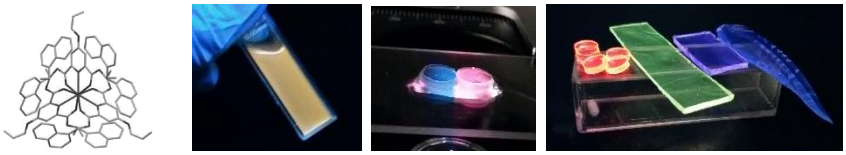
References:

1 Ocak, U.; Ocak, M.; Shen, X.; Surowiec and K.; Bartsch, R. A. *J. Fluoresc*, **2009**, 19(6), 997
2 Sutariya, P.G.; Pandya, A.; Lodha, A. and Menon, S.K. *Analyst*, **2013,** 138(9), 2531
3 Diao, H. *MSc Thesis NUIM*, **2013** and unpublished results
4 Maher, N. J. *PhD Thesis NUIM*, **2013** and unpublished results

Email: Justine.OSullivan.2009@mumail.ie

Self-Assembly for Luminescence: Ln(III)-coordination chemistry in generation of sensors and soft-materials

Samuel J. Bradberry*, Joseph P. Byrne, Colin P. McCoy, Thorfinnur Gunnlaugsson
School of Chemistry, Trinity College Dublin and School of Pharmacy, QUB



Abstract:

Materials with luminescent properties have technological importance across vast fields of science and technology with soft materials becoming of increasing value in biotechnology, chemical sensing and theranostics.[1] Coordination chemistry can, and does, play a key role in luminescent materials where coordination environments and ligand properties provide versatile optical[2] and structural property[3] variations. The 4*f*-elements are unique amongst emissive metals in that they have characteristic luminescence and versatile ligand design allows control of the metal-centred emission intrinsically and in response to multiple analytes.[4]

Incorporation into soft materials confers a number of scientific and economic advantages including: optical and structural enhancements with functional portability, facile fabrication and extremely low metal loadings.[5]

This talk will present our research towards the design and synthesis of soft materials, primarily gels and coordination polymers, through the self-assembly and incorporation of *4f*-metal complexes that are emissive and responsive into higher order materials. The interesting characteristics and emergent behaviours of these responsive luminescent soft materials will be explored and influences of coordination and supramolecular interactions will be discussed in the context of sensing, luminescence and mechanical properties.

References:

1 Noro, A., Hayashi, M. and Matsushita, Y., *Soft Matter*, **2012**, 8, 6416-6429
2 Kotova, O., Daly, R., dos Santos, C., Boese, M., Kruger, P.E., Boland, J.J. and Gunnlaugsson, T., *Angew. Chem. Int. Ed*., **2012**, 51, 7208-7212
3 Martinez-Calvo, M., Kotova, O., Mobius M.E., Bell, A.P., McCabe, T., Boland, J.J. and Gunnlaugsson, T., *J. Am. Chem. Soc.*, **2015**, 137, 1983-1992
4 Bradberry, S.J., Savyasachi, A.J., Martinez-Calvo, M. and Gunnlaugsson, T., *Coord. Chem. Rev.*, **2014**, 273-274, 226-24
5 McCoy, C.P., Stomeo, F., Plush, S.E. and Gunnlaugsson, T., *Chem. Mater.,* **2006**, 18, 4436-4343

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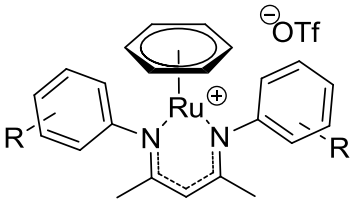
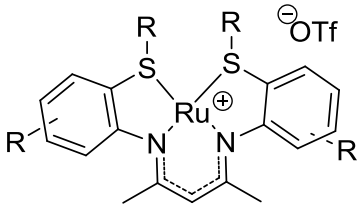
Flash Presentations

Ruthenium β-Diketiminate Complexes as Catalysts for the Rapid and Efficient Dehydrogenation of Amine Boranes

Phillips, A.D.; Grave, C.; Schreiber, D.F.; Lawlor, D. and O'Connor, C.*
Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland



(1)



(2)

Abstract:

A series of ruthenium complexes featuring the strongly chelating β-diketiminato ligand have been synthesised, characterised and evaluated as homogeneous catalysts for the rapid dehydrogenation of substrates of the type R_3NBH_3, where R = H or an alkyl group. These particular β-diketiminate-containing complexes have a unique ability to cleave H_2 heterolytically under mild conditions.[1-3] Employing both pressure and flow-meter measurements, variations in the substituent pattern of the flanking aryl group has a pronounced effect on H_2 release. Importantly, poisoning and related experiments reveals the homogeneous nature of these catalysts in the dehydrogenation process.[4]

The synthesis of two generations of catalysts based around the β-diketiminato ligand and their application as fast and efficient catalysts for amine borane dehydrogenation have been investigated. While the first generation (1) liberates an equivalent of H_2 from amine boranes in minutes, the second generation (2) has proved to demonstrate a faster dehydrogenation profile and more importantly, the ability to access a second equivalent of H_2 from ammonia borane at higher temperature.

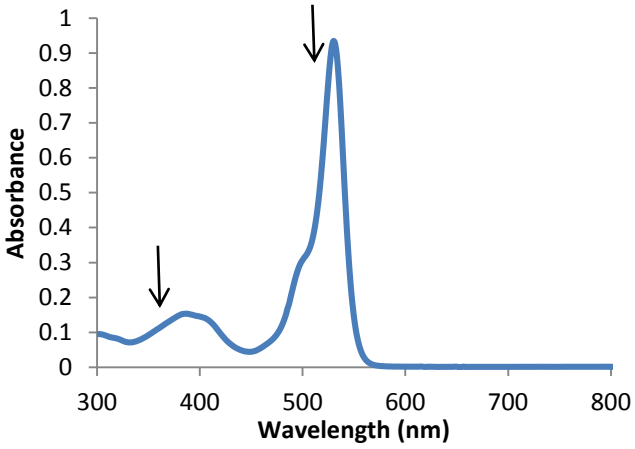
References:

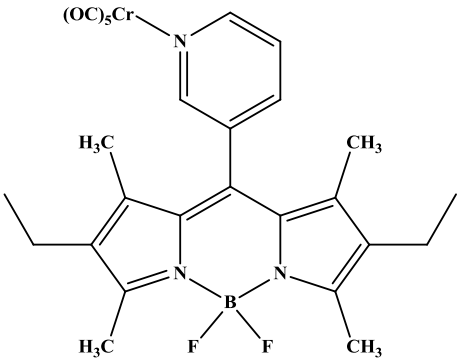
1 Phillips, A.D.; Laurenczy, G.; Scopelliti, R.; Dyson, P.J.; *Organometallics*, **2007**, 26, 1120.
2 Phillips, A.D.; Schreiber, D., *PCT Int Appl*, **2011**, WO 2011151792 A120111208.
3 Moreno, A.; Pregosin, P.S.; Laurenczy, G.; Phillips, A.D.; Dyson, P.J; *Organometallics*, **2009**, 28, 6432.
4 Schreiber, D.F.; O'Connor, C.; Grave, C.; Ortin, Y.; Müller-Bunz, H.;. Phillips, A.D.; *ACS Catalysis*. **2012**, 2, 2505.

Email: andrew.phillips@ucd.ie

The use of Fluorescent BODIPY Metal Carbonyls to Function as CO Releasing Molecules

McMahon,S. *; Kinahan A.; Hidalgo D. and Pryce, M.T.
Dublin City University





Abstract:

In recent years carbon monoxide (CO) has shown potential therapeutic effects due to its wide range of critical functions in the areas of inflammation, vasodilation, hypertension, neural transmission and organ graft rejection. CO releasing molecules (CO-RMs) have the means to transport and assist the delivery of defined amounts of CO to target areas in a safe and controlled manner.[1] A range of stimuli including thermal, photo- or electrochemical means, can be used to induce CO release in metal carbonyl compounds.[2]

A series of novel fluorescent BODIPY metal carbonyl complexes, incorporating both chromium and tungsten pentacarbonyls have been designed, synthesised and characterised. For example, the UV-vis spectrum and structure is shown above for the complex, 2,6-diethyl-1,3,5,7-tetramethyl-8-(3-pyridyl)-4,4'-difluoroboradiazaindacene chromium pentacarbonyl. The photochemical and photophysical properties have been investigated. Photochemically (indicated by the arrows at 355 nm and 525 nm), thermally (37 ^{o}C) and electrochemically induced CO loss were assessed via headspace analysis in conjunction with gas chromatography.

References:

1. Motterlini, R.; Clark, J. E.; Foresti, R.; Sarathchandra, P.;Mann, B. E. and Green, C. J. *Circ. Res.*, **2002**, 90(2), e17.
2. McMahon, S.; Rochford, J.; Halpin, Y.; Manton, J. C.; Harvey, E. C.; Greetham, G. M.; Clark, I. P.; Rooney, A. D.; Long, C. and Pryce, M. T. Phys. Chem. Chem. Phys. **2014**, 16, 21230.

.

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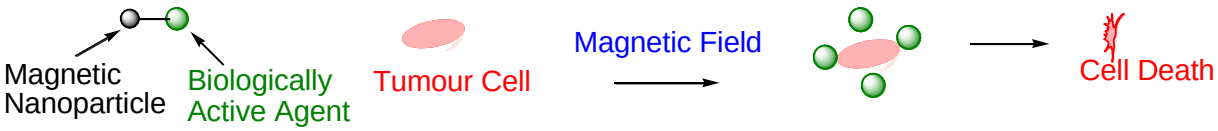
Novel Magnetic reservoirs for targeted drug delivery

*Mutuma, F.C.; Duffy, B. and Hargaden, G.C.
Dublin Institute of Technology



Scheme 1: Application of IONPs as Drug Delivery Agents

Abstract:

Conventional cancer drug delivery systems lack specifity; large doses of drugs need to be administered to achieve sufficient concentration for a therapeutic effect. Targeted drug delivery focuses on increasing the bioavailability of a drug at a specific part of the body for a duration of time. This reduces overall drug consumption thereby reducing costs and side effects. Iron Oxide Nanoparticles (IONPs) represent a significant class of inorganic nanomaterial that is contributing to the current revolution in targeted drug delivery. There is particular interest in using IONPs as drug delivery vehicles in cancer treatment to overcome problems associated with current invasive and non target specific methods. This research focuses on the synthesis of target specific medicinal agents with potential anti cancer activity, development of novel IONPs and study their use as drug delivery agents. The medicinal agents are analogues of *Gymnastatin*, a natural product that has shown potent cytotoxicity and growth inhibition against various cell lines. The medicinal agents will be evaluated for biological activity, coupled with our IONPs and the coupled adduct will be further evaluated for biological activity. Our method represents a short, efficient synthetic route to analogues of Gymnastatin. Gymnastatins alone would be efficient anti cancer agents and could have even greater potential as targeted drug delivery agents when coupled with IONPs.

References:

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2 Phoon, C.W.; Somanadhan, B.; Heng, S.C.H.; Ngo, A.; Ng, S.B.; Butler, M.S.; Buss, A.D.; Sim, M.M. *Tetrahedron* **2004**, *60*, 11619.

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Session B1
JH3
11.20 am – 1.00 pm

Oral Presentations

Combustion chemistry: Do we even understand how alkanes burn?

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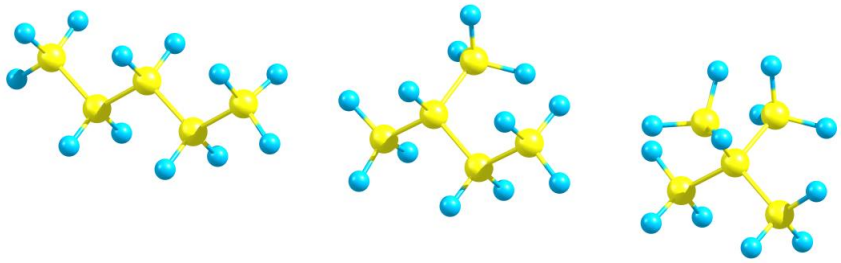

Abstract:

For several decades, detailed chemical kinetic models have been a useful tool in the development of combustion systems, such as internal combustion engines and gas turbines. Developing an understanding of combustion chemistry at the molecular level has helped drive combustor design in an efficient and cost effective way, and has been invaluable in the quest for higher efficiency and the reduction of harmful emissions.

A sizeable component of many fuels used in combustion applications is alkanes. Alkanes are the simplest type of hydrocarbon, so knowledge of the combustion of these compounds is essential to the fundamental understanding of the combustion of all hydrocarbons and other fuel types. The low-temperature (600–900 K) oxidation of alkanes is of practical importance to current internal combustion engine design, and also to advancement of more recent engine technologies such as homogeneous-charge compression-ignition (HCCI), premixed-charge compression-ignition (PCCI), and reactivity-controlled compression-ignition (RCCI) engines, as these systems typically operate over such temperature regimes.

However, despite the success of previous alkane models, problems existed. These mainly pertained to the mechanisms of the low-temperature oxidation pathways of these fuels, and the numerical values used within the models to describe their kinetic and thermodynamic properties. This work seeks to alleviate the existing discrepancies within the alkane models, utilising high-level quantum chemical studies in the literature. The pentane isomers are the focus of this study, as they are of a size which is practically manageable for a theoretical study, yet have structures that are complex enough to allow for the application of their kinetic, thermodynamic, and mechanistic rules to larger alkanes.

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Sequential immobilization of catalysts for application in cascade reactions:

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Abstract:

Immobilization of catalyst on solid supports can confer a number of advantages including ease of recovery and re-use and the capability of using biocatalysis in solutions such as in nonaqueous solvents, where the enzyme is insoluble [1, 2]. The use of mesoporous materials (MPS) as supports offers some valuable advantages and, more interestingly, can provide a more stable environment in comparison to planar surfaces. The large regular repeating porous structures of MPS enables the adsorption of high loadings of catalytically active enzymes within the pores. Individually optimized heterogeneous catalysts such as metal based catalysts and enzymes can be prepared and combined for use in cascade reactions.

We have developed a detailed protocol for the successful immobilisation of enzymes on MPS [3] including lipase CALB [4], glucose oxidase and alanine racemase [5]. Here we report the preparation of styrene oxide using a chemo-enzymatic cascade system. The catalytic system involves the enantioselective epoxidation of styrene by manganese complexes (1,4-dimethyl-1,4,7-triazacyclononane) using H_2O_2 generated by immobilized glucose oxidase. The intermediate styrene oxide can then be further converted to amino-phenylethanol by haloalcohol dehalogenase.

References:

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[4] N.H. Abdallah, M. Schlumpberger, D.A. Gaffney, J.P. Hanrahan, J.M. Tobin, E. Magner, Journal of Molecular Catalysis B: Enzymatic, 108 (2014) 82-88.
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Detection of Single Base Substitutions in 25-mer Oligonucleotides Using Surface-enhanced Raman Spectroscopy

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Abstract:

Methods for detection of specific short DNA sequences using surface-enhanced Raman spectroscopy have concentrated on approaches where the target sequence is somehow attached to a strongly scattering label and it is the signal from the label which is detected in the assay. An attractive alternative approach is to use the intrinsic Raman signal of the bases in the sequence, which has the advantage that it does not require an extrinsic label to be attached to the target. However, some previous studies have cast doubt on the practicality of such an approach e.g. by reporting spectra which do not change significantly with the base sequence. Nonetheless, we have previously shown that the substitution of a single base at the end of a 25-mer sequence could be detected using SERS difference spectra.[1] Here we have extended that study by using an extended series of 11 unthiolated 25-mer oligonucleotides with single base substitutions at the 3', 5' ends and the centre of the sequences.

The SERS spectra of the 25-mer ss-DNA sequences were highly reproducible, which allowed reliable difference signals to be obtained by 1:1 subtraction. In most cases the difference spectra showed the expected changes with base substitution but some difference spectra deviated strongly from the expected form. It was found that in the cases where these anomalous effects were observed they could be removed by gently heating to 60°C for 15 min before recording the spectra, implying that they are due to specific DNA folding of some of the sequences which causes non-representative (but still highly reproducible) spectra to be obtained.

In general, provided the samples were uncoiled before being measured, the same types of base substitutions gave similar SERS difference spectra, irrespective of whether the exchanged bases were at either end or the centre, i.e. there were no end effects of the type reported for thiolated ss-DNA. This demonstrates that the SERS spectra of oligonucelotides up to at least 25 bases contain detectable contributions from all bases in the sequences. This is important for both sequence identification and detection of post-transcription base modifications which can randomly occur at any point along the chain.

References:

1 Barhoumi, A. and Halas, N. J. *J. Phys. Chem. Lett.*, **2011**, 2, 3118.
2 Papadopoulou, E. and Bell, S.E.J. *Angew. Chem. Int. Ed.*, **2011**, 50, 9058.

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Flash Presentations

Targeted β-phase formation in poly(fluorene)-ureasil grafted organic-inorganic hybrids

Meazzini, I.[1]*; Behrendt, J.M.[2]; Turner, M.L[2] and Evans, R.C.[1]
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[2]*School of Chemistry, University of Manchester, UK*

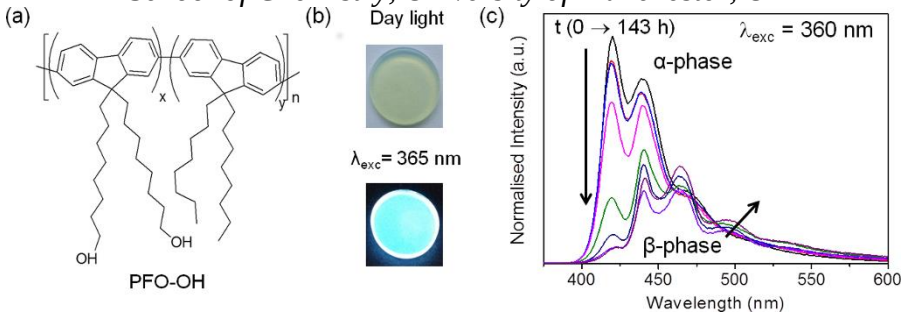

Figure 1. Structure of PFO-OH (a), a PF-TU hybrid under day light and UV irradiation (b) and the evolution of the emission profile a PF-DU during the sol-gel process (c).

Poly(fluorenes) (PFs) have emerged as an important class of materials for application in polymer light-emitting diodes (PLEDs).[1] Based on their state of aggregation, PFs exist in three different phases: the amorphous α-phase, the π-stacked β-phase and the 3D-network γ-phase. Controlling the formation of the β-phase is of key interest as the opto-physical properties of PFs depend on their conformation.[2] Targeted β-phase formation has previously been achieved through modulation of the PF side-chains,[3] or by controlling the interaction between the PF and the host material through self-assembly.[4] Here, we investigate the targeted formation of the PF β-phase through the covalent-grafting of a poly[(9,9-dioctylfluorene)-*co*-(9,9-bis(8-hydroxyoctyl)fluorene)] (PFO-OH) copolymer (Fig.1(a)) with two distinct siloxane–polyether hybrids, whose precursors present different degrees of branching, using sol-gel chemistry. The resulting PF-diureasils (PF-DUs) and PF-triureasils (PF-TUs) are obtained as transparent monoliths (Fig.1(b)). Optical studies on PFO-OH in THF reveal a vibronically-structured emission band from 400-500 nm and a broad excitation band centred at 380 nm, characteristic of PF in the disordered α-phase. During the sol-gel reaction, as the silica network condenses, the PF chains undergo a conformational change guided by a combination of non-covalent interactions leading to the formation of the more planar β-phase.[2] β-phase formation is confirmed by its unique optical fingerprint: a 20 nm red-shift in the emission maximum (Fig.1(c)) and the emergence of a peak at 435 nm in the excitation spectrum. These results indicate that the ureasil structure induces distinct levels of control over the β-phase packing, promoting different vibronic transitions, and representing a promising step towards the creation of new PF-ureasil materials with tailored optical properties.

References:

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2 Knaapila, M. and Monkman, A.P. *Adv. Mater.*, **2013**, 25(8), 1090.
3 Evans, R.C. and Marr, P.C. *Chem. Commun.*, **2012**, 48(31), 3742.
4 Behrendt, J.M.; Wang, Y.; Willcock, H.; Wall, L.; McCairn, M.C.; O'Reilly, R. and Turner, M.L. *Polym. Chem.* **2013**, 4(5), 1333.

Effect of the Presence of MEA on the CO_2 Capture of Superbase Ionic Liquids

McCrellis,C.*; Taylor, S.F.R.; Jacquemin, J. and Hardacre,C.
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Abstract:

Recently, efficient CO_2 capture and release has been demonstrated by a set of phosphonium superbase ionic liquids.[1] Further investigation of these promising results has been carried out; including the effect of modifying the cation as well as the study of other superbase anions.[2] In our studies both gravimetric and volumetric methods have been used to quantify and investigate the CO_2 capture of selected ionic liquid-based solutions. To date, literature studies have focused on CO_2 capture under dry conditions, however for the application of CO_2 capture from flue gas it is important to understand the effect of water on the CO_2 uptake. In this work, the effect of water on the CO_2 capture of $[P_{666,14}]$[124Triz], $[P_{666,14}]$[PhO], $[P_{666,14}]$[Bentriz], $[P_{666,14}]$[123Triz] and $[P_{666,14}]$[Benzim] has been evaluated showing that depending on the anion, water can have a positive or negative effect on the CO_2 uptake.[2] As well as studying the effect of water, the effect of the addition of monoethanolamine (MEA) as a solvent has been investigated extensively. Currently in the literature the effect of MEA as an added solvent on CO_2 absorption has only been investigated using ILs that physically absorb the CO_2. These studies show that the MEA has no prominent effect on the CO_2 uptake however, it does have an effect on the rate of uptake.[3,4] This is due to the decrease in viscosity on the addition of a solvent. In this work, we investigated this effect when the MEA is added to ILs that chemically absorb the CO_2. Initial results have shown that generally the presence of MEA has the ability to enhance the CO_2 capture in these media suggesting that both the IL and MEA are working synergistically.

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Growth of tin seeded multi-segment silicon-germanium axial heterostructure nanowires in a wet chemical solvent vapour growth system

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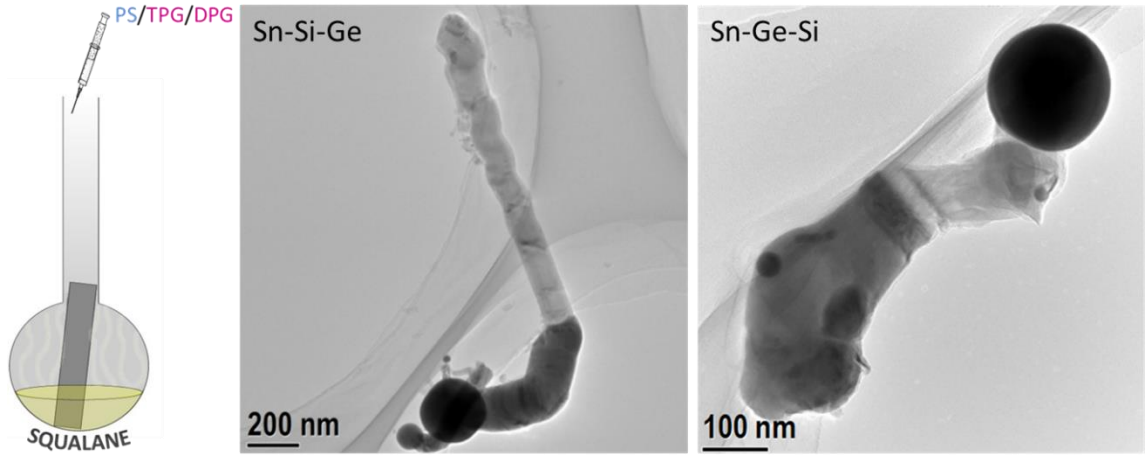

Abstract:

Silicon (Si) and germanium (Ge) nanowires (NWs) are very promising materials for their use in applications such as energy storage, transistors and photovoltaics. Compound semiconductor NWs are of particular interest for their potential use in high performance devices. Herein, we present the high density growth of multi-segment axial Si-Ge heterostructure NWs in a versatile, low cost glassware system, where the vapour phase of a high boiling point solvent acts as the growth medium. A variety of heterostructure NW combinations can be grown using this system, including Si-Ge, Ge-Si, Si-Ge-Si, Ge-Si-Ge as well as double and triple Si-Ge, with minimal alloying observed at the Si-Ge interfaces. An evaporated layer of tin (Sn), on stainless steel was chosen as the growth substrate. Sn was chosen as it is a low solubility type B catalyst which allows for the production of highly abrupt interfaces between the Si and Ge segments. The length of each Si and Ge segment can also be controlled in this system by carefully controlling the reaction time. These NWs are characterised using high resolution transmission electron microscopy (HRTEM), dark field scanning transmission electron microscopy (DF-STEM) and energy dispersive X-ray analysis (EDX), with aberration corrected scanning transmission electron microscopy allowing for determination of the interfacial abruptness between the Si and Ge segments. This growth system can also be extended for the growth of these structures using other type B catalysts such as indium and bismuth.

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Session A2
JH2
2.40 pm – 3.55 pm

Academic Presentation

Novel approaches to luminescent solar concentrator design using organic-inorganic hybrid waveguides

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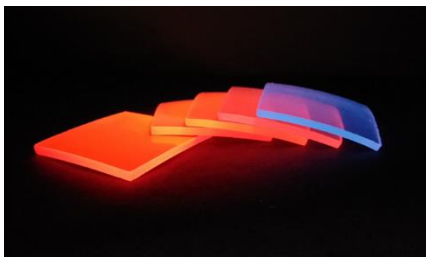

Abstract:

Luminescent solar concentrators (LSCs) can decrease the cost of solar power by reducing the number of solar cells required. The classic LSC design consists of a transparent waveguide plate that contains, or is coated with, lumophores that absorb sunlight and re-emit it at energies that match the band gap of an attached solar cell.[1] The LSC efficiency depends on the spectral properties of the lumophore and the waveguide, as well as the device architecture.[2] In this talk, recent progress from our group towards the design and fabrication of novel hybrid organic-inorganic LSC architectures will be described. It will be demonstrated that light-harvesting and concentration can be significantly improved by tailoring the optical properties and orientation of the lumophore and waveguide.

Particular focus will be placed on organic-inorganic ureasil hybrid waveguides prepared by sol-gel processing, incorporating both for organic dyes and conjugated polymers as the lumophore.[3] It will be shown that ureasils are superior waveguides to polyacrylates due to their optimum refractive index and high transmittance. Moreover, their processability allows us to examine the efficiency of three LSC architectures: a thin film LSC (TLSC), a doped LSC (DLSC) and a new hybrid LSC construct (HLSC) in which a thin film of the lumophore is confined below the waveguide surface. Finally, it will be revealed that by covalently grafting the lumophore to the waveguide, it is possible to control the self-organisation of the lumophore and thus its optical properties. Our results demonstrate that organic-inorganic di-ureasil polymers are excellent waveguides for LSCs and that LSC-coupled cells are a viable alternative to enhance the performance of solar technologies.

References:

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4. Evans, R. C., *J. Mater. Chem. C*, **2013**, 1, 4190.

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Oral Presentations

Hydrogen Bonding and its Effect on Alkoxysilane Condensation

Killian Barton[1], Brendan Duffy[1], Brendan Kneafsey[2], Eimear Fleming[2] and Deirdre Ledwith[2]

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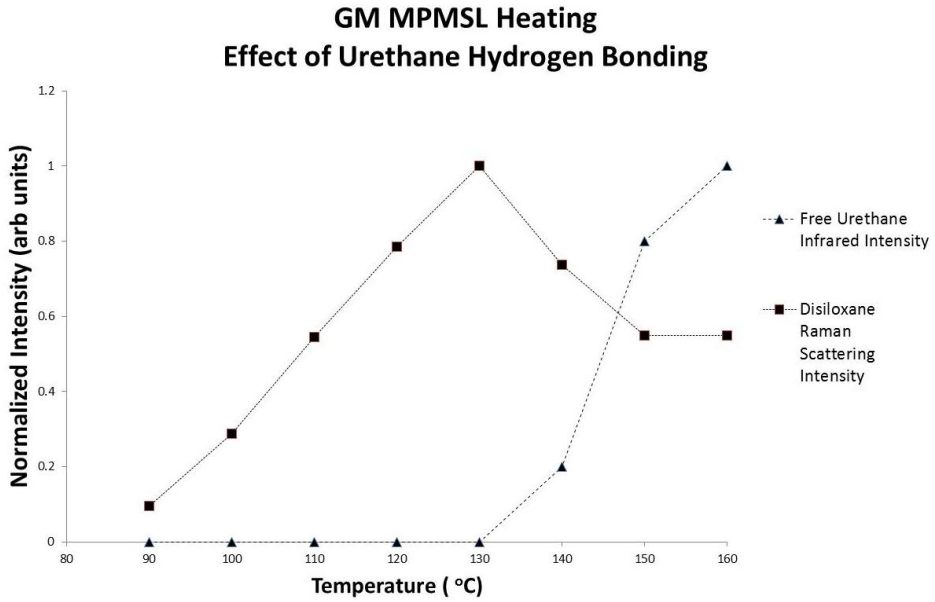

Figure 1: Temperature dependence of condensation of GM and free urethane formation

Abstract:

The temperature dependent chemical changes of an alkoxysilane based rubber to metal bonding agent were analysed using vibrational spectroscopy. Raman and infrared spectroscopy allowed for the identification the condensation behaviour of the alkoxysilane and the secondary amine based hydrogen bonding respectively[1]. Analysis was carried out as a function of temperature. This reflects the high temperature conditions of the application environment in which the bonding agent is used. Both features are believed to be associated, *ie* the urethane hydrogen bonding is thought to be responsible for controlling the condensation behaviour of the alkoxysilane. Adhesion testing has been carried out and the vibrational data will be discussed in the context of the preliminary adhesion results.

References:

1. Boyarchuk, Y., and L. Rappoport, *Polym. Sci. U.S.S.R.* (1965): pp. 778–785.

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Investigation of phospholipid conditioning of carbon surfaces for applications in biomaterials

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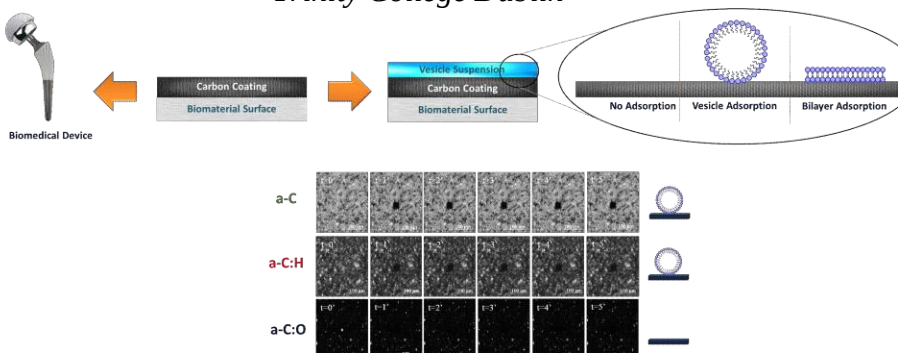

Abstract:

Lipids are key components in biological systems, acting as a structural element of cells and being responsible for signalling and storing energy. As surface active compounds, lipids can self-assemble at solid surfaces as intact vesicles or lipid sheets[1]. Understanding how lipids interact with materials and what is their role in determining the physiological response to a biomaterial will contribute to our ability to prevent undesirable bioresponses. Carbon materials, nanomaterials and coatings are currently under intense study for biomaterial and biodevice applications[2]; here we report a study on the interactions between model lipid assemblies and carbon surfaces. The adsorption of phosphatidylcholine (PC) / phosphatidylserine (PS) liposomes onto amorphous carbon surfaces was investigated as a function of pH. We used Infrared Reflectance Spectroscopy (IRRAS) measurements to determine whether PC/PS liposomes adsorb at carbons with different surface chemistry and surface free energy. We also used fluorescence imaging and fluorescence recovery after photobleaching (FRAP) methods in order to understand the mode of adsorption, in particular whether liposomes undergo rupture upon adsorption. Our results suggest that surface modification of carbon can be used to tune the mode of adsorption, a result that has implications for applications of carbon materials and nanomaterials in biology.

References:

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Session B2
JH3
2.40 pm – 3.55 pm

Academic Presentation

Bio-Inspired Active Fluidic Systems based on Stimuli-Responsive Materials

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Abstract:

The 1980s vision of low-cost autonomous chem/bio-sensing devices that can function reliably for years as components of implanted artificial organs, or as building blocks of widely distributed environmental sensor networks remains unrealised, despite huge investments in research effort and resources. In the 1990s, it was expected that microfluidics would provide a solution, by enabling advanced functions like calibration and sample processing to be integrated into a small, potentially mass produced chip [1]. However, microfluidics essentially emerged from semiconductor fabrication technologies, and was based on principles largely borrowed from the hugely successful microelectronics industry. Today, the dominant use model for chem/bio-sensors is 'use once and discard', and while this can be relatively reliable, it normally involves manual sampling and is not a scalable model [2].

In recent years, the area of stimuli-responsive materials has grown rapidly, and many different modes of action have been demosntrated. In this paper, I will focus mainly, but not exclusively, on photo-responisve soft gels and micro-vehicles based on hydrophobic droplets and show how they could be incorporated into microfluidic systems to replicate (albeit in a primitive way) some functions of our own biological circulation systems [3]. Through such concpets, it may be possible to create futuristic analytical devices in which the fluidic system is much more than a means to transport samples and reagents to a detector. Rather, it becomes an active component in the device, capable of performing advanced functions like system status checking, leak/damage detection and self-repair/maintenance. In this manner, it may be possible to dramatically extend the functional lifetime of anaytical devices far beyond the current state of the art, and make progress towards relaising the 1980s vision for chem/bio-sensors.

References:

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Oral Presentations

Development of chemically modified screen printed carbon electrodes for caffeine and mouse IgG detection

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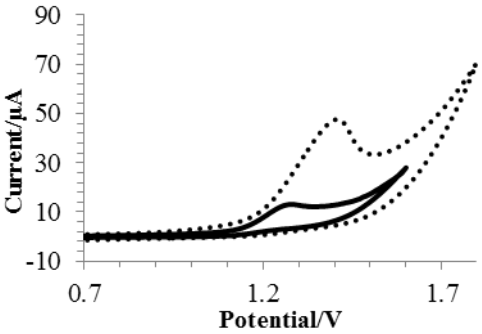

Fig.1. Electrochemical detection of caffeine: comparison of bare graphite electrode and nafion modified electrode (dotted line).

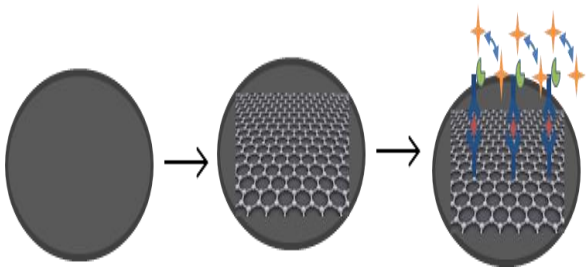

Fig.2. Scheme for the development of a graphene modified screen printed electrode for the detection as mouse IgG

Abstract:

The use of sensor technology in food analysis has gained a large amount of interest in recent years [1]. In this work, two different sensing strategies are outlined. Firstly, a chemical sensor for the detection of caffeine in real samples has been developed. As caffeine is an electrochemically active compound it can be detected directly using voltammetric methods. Graphene oxide, electrochemically reduced graphene oxide and nafion were then used to investigate the possibility of improving sensor sensitivity. It was found that the nafion modified electrode exhibited the best electroanalytical characteristics. These electrodes were then used in the development of an electrochemical immunosensor, using mouse IgG as a model analyte. This assay was then compared to the conventional ELISA technique and evaluated for use as a sensor for mycotoxin detection. Mycotoxins are secondary metabolites produced by a range of fungi and molds which have been linked to mutagenicity, teratogenicity and carcinogenicity in humans. Screen printed carbon electrodes have been used in this work because of their low cost which makes them a viable solution in industrial applications [2].

References:

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2 Ricci, F; Adonetto, G; Palleschi, G, *Anal Chim Acta*, **2012**, 605(2),111

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Development of a Biosensor for the Real Time Neurochemical Monitoring of Superoxide

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Abstract:

Superoxide anion (O_2^-) is the primary species of the reactive oxygen species (ROS) and is generated as a reduced intermediate of molecular oxygen [1]. O_2^- in biological samples lies within the narrow range of 50-200nM [2]. When their production exceeds the body's natural ability to deal with these potentially cytotoxic species a variety of pathological conditions may occur including stroke, cancer and neurodegeneration [3]. The objective of this research is the development of a novel biosensor to detect O_2^- using long term *in-vivo* electrochemistry (LIVE). LIVE requires a micro sensor to be implanted into a specific brain region and local changes in the concentration of substances to be monitored with sub-second time resolutions over extended periods (Figure 1). Experiments were performed using a standard three electrode cell consisting of a working reference (Saturated Calomel Electrode (SCE)) and an auxiliary electrode (silver wire) in 5mL of Phosphate Buffer Solution (pH 7.4) containing 0.002U of xanthine oxidase in a glass electrochemical cell. Experiments were performed using constant potential amperometry (CPA) at +700mV vs. SCE. The optimum sensor design thus far is Pt/SOD/0.5%GA/2%PEI which has a linear region slope of 0.91± 0.06 nA/µM (n = 17) showing that this sensor displays a high sensitivity to superoxide at physiological levels.

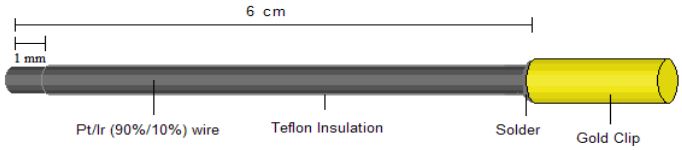

Figure 1: A microsensor suitable for neurochemical monitoring of superoxide

References:

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Session A3
JH2
4.40 pm – 5.50 pm

Oral Presentations

Improved High Temperature Stability of Anatase TiO_2 Photocatalysts

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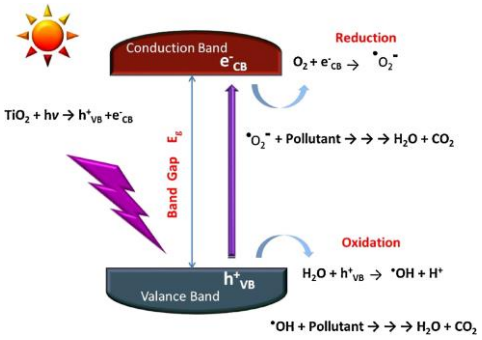

Figure 1. Schematic of the mechanism of TiO_2 photocatalysis.[1]

Abstract:

Among the three common phases of TiO_2 (anatase, rutile, and brookite), the anatase form is reported to be the best photocatalyst due to the improved charge-carrier mobility and the greater number of surface hydroxyl groups. The anatase to rutile transition in titania photocatalysts usually occurs at a temperature between 600 °C to 700 °C.[2] Development of a high temperature stable (above 1000 °C) anatase phase is important for various environmental applications (*e.g.* self-cleaning ceramic tiles, anti-microbial sanitary wares *etc.*), which require the use of very high temperatures during their processing stages.[3] Modification of the TiO_2 structure to increase the efficiency of the material is important. Modified TiO_2 can differ from standard TiO_2 in several ways including crystalline phase, light adsorption, surface structure, rate of electron-hole recombination and adsorption of substrates. The addition of dopants to alter the band-gap of anatase to allow the utilisation of visible light (40 %) compared to UV light (4-5 %) of the solar spectrum is studied. It is possible to develop quite different TiO_2 materials by variation of parameters such as dopant type, dopant ratio and calcination temperature. Some dopants of interest to be discussed are nitrogen, fluorine, phosphorous and carbon. The samples prepared at various concentrations of dopant were characterised using XRD, Raman, FT-IR and diffuse absorbance spectroscopy. The photocatalytic activity of the materials prepared was investigated by measuring the decomposition rates of a model compound, Rhodamine 6G, using simulated solar irradiation.

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Mechanism and Kinetics of Advantaged Biofuels Synthesis from D-Fructose

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Abstract:

The advanced lignocellulose derived biofuel candidates, ethyl levulinate and 5-ethoxy methyl furfural, are synthesised from α/β-d-fructopyranose (d-fructose) in a condensed phase homogeneous ethanol system catalysed by hydrogen cations. The detailed study of the d-fructose hydrolysis mechanism is important as it is a recognised bottle-neck species, connecting lignocellulose derived glucose to the feasible production of biofuels. A mechanistic comprehension is pursued by detailed measurements of the reactant, intermediate and product species evolved with time, as a function of H_2SO_4 (0.09 M, 0.22 M, 0.32 M) and d-fructose concentration (0.14 M, 0.29 M, 0.43 M), also considering the addition of water to the ethanol media (0/100, 12/88, 24/76 weight %). d-fructose, 5-hydroxy methyl furfural, 5-ethoxy methyl furfural, ethyl levulinate, and ethyl fructoside species, are quantified as major species fractions, summing to 45-85 % of the initial d-fructose mass.

This information and pertinent findings from the literature are utilised to assemble incremental mechanistic propositions, to account for the synthetic system. Ten empirical reactions are considered, assuming a first order relationship to the hydrogen cation concentration for each. To test each mechanistic proposition, these reactions are assembled into mass-conserved chemically authentic kinetic models and empirical rate constants are derived for each of the chemical reactions considered. The model indicates that d-fructose is unlikely to undergo direct hydrolysis to 5-hydroxy methyl furfural and that the reaction pathway likely proceeds through a stable (fructofuranose or anhydro fructofuranose) intermediate. This study notes that detailed investigations of the initial fate of d-fructose reaction in ethanol limits further mechanistic comprehension.

Using the reaction mechanism, for the optimal condition studied, the synthesised fractions of ethyl levulinate, 5-ethoxy methyl furfural and 5-hydroxy methyl furfural, considered as fuel components, achieve a volumetric energy valorisation ($\Delta H_{Combustion}$, kj/ml) of 312 % with respect to the ethanol consumed, indicating the technical viability of the process.

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Flash Presentations

Derivatised Phens: The Quest for New Anti-Tuberculosis Drugs

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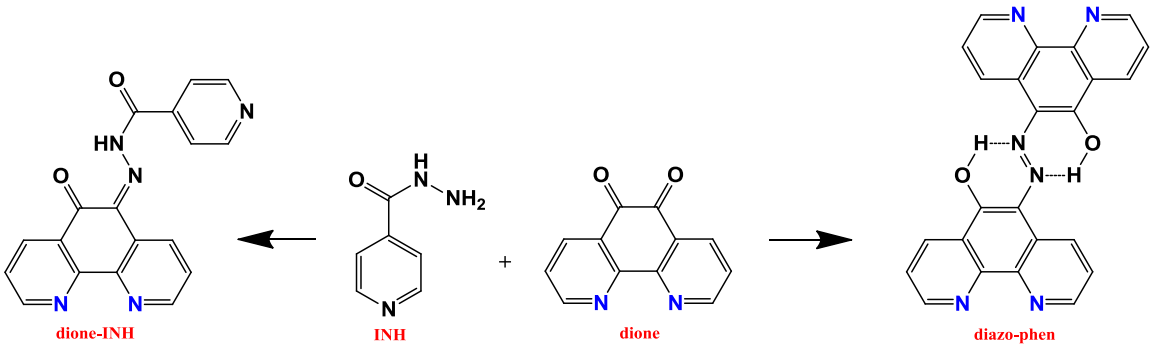

Fig 1: Reaction of INH with dione to give dione-INH and diaza-phen.

Abstract:

Tuberculosis (TB), caused by the bacterium *Mycobacterium tuberculosis*, causes 1.7 million deaths annuallly.[1] TB treatment comprises of a mixture of isoniazid (INH), rifampicin, pyrazinamide and ethambutol, administered over six months. The prevalence of multidrug resistant-TB (MDR-TB) and extensively drug resistant-TB (XDR-TB) strains have accelerated the search for low cost drugs with improved efficacies and reduced side effects.

Recently, we have synthesised an array of manganese(II) 1,10-phenanthroline complexes which exhibit anti-*M. tuberculosis* activity in the nano- to micro-molar range.[2] A continuance of this work is presented here. Details of the synthesis and characterization of two novel organic metal chelating ligands (Fig. 1) formed by reacting INH with 1,10-phenanthroline-5,6-dione (dione). Preparation of the Mn(II) complexes will also be given.

References:

1 World Health Organisation. *Tuberculosis Fact Sheet, 2014.* Available from: http://www.who.int/mediacentre/factsheets/fs104/en/. Accessed: 7th May 2015.

2 McCann, M., Devereux, M. et al. Unpublished work.

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Bismuth Hydroxamic Acid Complexes as Potential anti-*H. pylori* Agents

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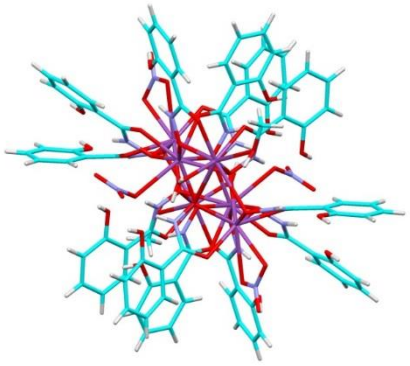

Abstract:

Helicobacter pylori is a microaerophilic and neutralophilic Gram Negative bacterial pathogen that colonises the human stomach and is associated with gastrointestinal disorders including dyspepsia, peptic ulcers and is the strongest known risk factor associated with gastric cancer. Recently H. pylori has been associated with a growing number of extragastric conditions such as iron deficiency anaemia, Parkinson's disease and heart disease. Rates of H. pylori infection are currently estimated to be 20-50% in industrialised nations and up to 80% in developing countries.(1) This bacteria utilises a process called acid acclimation, in which the Urease enzyme plays an important role in the bacteria's ability to colonising the harsh environment of the stomach

The continuing rise in antibiotic resistance has caused a marked decrease in the efficacy of standard first line treatments for H. pylori and despite concerted effort to select suitable drugs and tailor parameters such as dosage, dosing intervals and treatment duration an effective treatment regimen for H. pylori has not been established yet. There is therefore an urgent need to develop novel strategies for effectively combating H. pylori.

Progress in relation to the development of novel bismuth hydroxamic acid complexes as potential anti-H. pylori agents will be reported. These compounds will target H. pylori via two independent mechanisms; the well-known bactericidal activity of bismuth(III) ions and inhibition of urease via hydroxamic acids.

References:

1 Keogan DM, Griffith DM. Molecules. 2014; 19: 15258-15297.

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Session B3
JH3
4.40 pm – 5.50 pm

Oral Presentations

TOXOR: Design and Application of an Electrochemical Toxicity Biosensor for Environmental Monitoring

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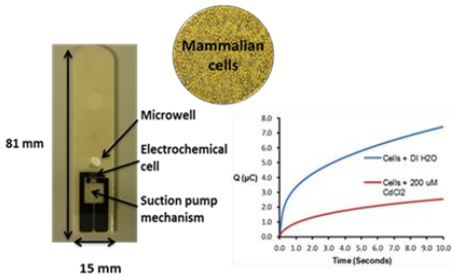

Figure 1 Electrochemical measurement of toxic $CdCl_2$ using TOXOR Biosensor

Abstract:

Here we present design and assay methodology for a novel electrochemical biosensor with the view to assess cytotoxic effects of key chemicals. The device is based on mammalian cells as the biological recognition agent (A549 human lung epithelial cells) and measurement of changes in cellular enzyme (acid phosphatase – AP) following exposure to toxic chemicals. AP catalyses the de-phosphorylation of 2-naphthyl phosphate to 2-naphthol (determined by chronocoulometry) and is indicative of metabolically active cells. Immobilised living cells exposed to pentachlorophenol, cadmium chloride and nickel chloride exhibited a decrease in AP activity which enabled IC_{50} (50 % reduction in enzyme activity) values of toxic chemicals to be determined by electronic detection (Fig. 1). The biosensor has also been employed for nanotoxicity screening applications with mercaptosuccinic acid coated CdTe quantum dots employed as a model nanotoxin. At present work is underway to improve the storage stability of the biosensor by employing fish cells as the biological recognition agent. It is envisaged that this device could be exploited in the screening of industrial and environmental toxins and has potential in pharma/drug testing applications.

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Implantable pH sensors for monitoring of oral health in the elderly

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3 School of Mechanical & Materials Engineering, Engineering Building, Belfield, Dublin

Abstract:

*corresponding author

This research is focused on the development of implantable electrochemical-based oral sensors which will monitor oral disease in the elderly (1), by detecting changes in salivary pH and gingival tissue temperature. This paper describes the characterization studies which were carried out on both pH sensors in phosphate buffer solutions and artificial saliva (AS). A salivary pH of between 4.5pH and 7.5pH (2), and gingival temperature between 35°C - 38°C (3), were identified as the target range of interest for the human oral environment. The pH sensors used, were a gold electrode with a pH sensitive iridium oxide (IrOx) layer grown *via* continuous cyclic voltammetry (4), and an Ion Sensitive Field Effect Transistor (ISFET) probe (5). Sensor measurements were recorded in solutions of varying pH and temperature. An ISFET probe was then implanted into a prototype denture and re-tested in AS, at varying pH levels and temperatures. The implanted ISFET probe responded linearly but at a lower output potential than the non-encapsulated ISFET. Normalisation of the output data could be carried out during signal processing design to account for this error. This study demonstrates the suitability of ISFET and gold electrode pH sensors for incorporation into implantable oral sensors.

References:

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3. Kung RT, Ochs B, Goodson JM. Temperature as a periodontal diagnostic. *J Clin Periodontol*. **1990** Sep;17(8):557–63.
4. Hu J, Abdelsalam M, Bartlett P, Cole R, Sugawara Y, Baumberg J, et al. Electrodeposition of highly ordered macroporous iridium oxide through self-assembled colloidal templates. *J Mater Chem*. **2009** Jun 3;19(23):3855–8.
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Flash Presentations

Vapour phase methods for inclusion of inorganic materials into block copolymer patterns

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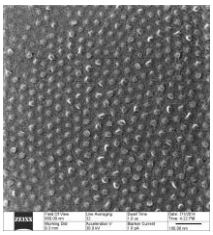

TiO_2 nanodots formed by vapour phase inclusion into a PS-b-PEO nanopatterns

Abstract:

Block copolymers are macromolecules where distinct chemical blocks are present and are covalently linked. If the blocks are substantially chemically different, these systems will phase separate. However, the phase separation is frustrated by the chemical bonds between blocks ensuring that the phase separation occurs into distinct nanopatterns that minimize interactions between blocks. This form of self-assembly is known as microphase separation and in favourable circumstances can yield arrangements at substrates that have close to lithographic dimension and periodicity. This has led to these materials being seen as potential solutions to scaling challenges in the microelectronic fabrication industry.

However, the pattern has little practical use and must be converted into an inorganic structure be either pattern transfer (using the pattern as a mask) or by selected inclusion into one of the blocks where the polymer acts as a template. Here we report work on the polystyrene-b-polyethylene oxide (PS-b-PEO) as a template for nanodimensioned TiO_2 formation. Using volatile titanium precursors, titanium ions are selectively introduced into the PEO block of well-defined PS-b-PEO structures. Simple UV-ozone exposure renders an inorganic mimic of the polymer pattern. By control of exposure time, temperature and humidity, fidelity between the titania structure and the original BCP pattern can be defined. This work reports the details of the methodology and the structural and spectroscopic analysis of the nanopatterns.

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Polymorphism in two Model Active Pharmaceutical Ingredients

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School of Chemistry, National University of Ireland, Galway, Ireland

Abstract:

Polymorphism is the ability of a compound to appear in two or more crystalline structures. Different polymorphs have different physical and chemical properties due to differences in the dimension, shape, symmetry, and void volumes of their unit cells. Differences in the packing properties and intermolecular interactions lead to differences in mechanical properties. Thus, polymorphism is extremely interesting and relevant to the pharmaceutical industry because it can directly affect properties such as solubility, stability and bioavailability of active pharmaceutical ingredients (APIs).[1]

In this study we studied the polymorphism of two model APIs, p-aminobenzoic acid and benzamidinium salts. P-aminobenzoic acid(PABA) has been selected in this study as it contains CO(OH) and NH_2 functional groups that can donate and accept H-bonds. PABA has two different polymorphs, α (needles) and β (prism shape). The most stable polymorph is β form, So far there are so difficulties to getting β form as pure crystals. In this study we developed a method to have the β form in pure quality.

[2] The amidine functional group ($RC(=NH)NH_2$) of benzamidine is an important pharmacophore that is present in a large number of drugs and pharmaceuticals. Amidines display a variety of pharmacological activities and have different applications.[3] They are strong bases and are usually protonated under physiological conditions. The positively charged amidinium group has four protons that can form strong charge-assisted hydrogen bonds. Benzamidinium hydrogen maleate crystallizes as large needles of up to > 3 cm length. Attempts to influence the crystal habit and size through a change of solvent and the presence of additives yielded a second polymorph. The formation and conversion of the two polymorphs by mechanochemistry was also investigated.[5] Mechanochemistry has recently been recognized as an attractive alternative to the traditional solution crystallization method.[4] Ball-milling of benzamidine with sulfamerazine generated amorphous benzamidinium sulfamerazinate that crystallized to a crystalline that was different from that obtained by solution crystallization.

References:

[1] Harry G. Brittain, Polymorphism in pharmaceutical solids, CRC Press, 2009 and refs therein.
[2] Sandra Gracin,; Ake C.Rasmusen. Crystal growth& Design 2004, 4, 1013-1023.
[3] Perrine, D; Georges, P.; Lancelot, J. C.; Saturni. Agents Chemother. 1995, 39, 339–342.; Fuertes, M. A.;. Chem. Biodivers. 2005, 2, 1387–1400; Nehrbass-Stuedli, A.; Brun, R. *Antimicrob. Agents Chemother.* 2011, 55, 3439–3445.; Boykin, D. W. Expert Opin. Ther. Patents 2007, 17, 927–939.
[4] James, S. L.; Adams, C. J.; Bolm, C.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; A. G.; Parkin, I. P.;; Waddell, D. C. Chem. Soc. Rev. 2012, 41, 413–447.
[5] N. Kamali, M. Aljohani, P. McArdle, A. Erxleben, submitted

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Session A4
JH2
10.00 am – 12.35 pm

Oral Presentations

Imidazolium and Pyridinium Ionic Liquids from Mandelic Acid; Synthesis, Biodegradation and Toxicity Evaluation

Prydderch, H.[1,*]; Ventura, S. P. M.[2]; Ghavre, M.[1]; Ferreira, F. M. M.[2]; Gonçalves, F.[2]; Quilty B.[3]; Coutinho, J. A. P.[2]; Špulák, M.[4]; Haiß, A.[5]; Kümmerer, K.[5] and Gathergood, N.[6]

[1]*School of Chemical Sciences, Dublin City University, Ireland*
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[4]*Department of Inorganic and Organic Chemistry, Charles University, Czech Republic*
[5]*Institute of Sustainable and Environmental Chemistry, Leuphana University Luneburg, Germany*
[6]*Department of Chemistry, Tallinn University of Technology, Estonia*

Abstract:

Ionic liquids (ILs) are often described as 'green solvents'; mainly due to their very low vapour pressure. However, assessment of their environmental impact is also a requirement. It is desirable that ILs do not persist in the environment and should have low toxicity to a broad range of organisms. This is a challenging goal for IL research today. The work of the Gathergood research group is aimed towards the synthesis and analysis of biodegradable[1], low toxicity ILs[2] and their applications[3].

The Gathergood group has proposed that using renewable resources to form ILs could improve the eco-toxicity and biodegradability of the compounds. Thus, work has been carried out on the synthesis of ILs with a bio-derived cation, namely mandelic acid. Initially a series of eight ILs from substituted mandelic acid derivatives with imidazolium and pyridinium headgroups were synthesised. This allowed for the investigation of toxicity on modifying the heterocycle, aromatic ring substitution, ester group, and proximity of cation to aromatic ring[3].

Two pyridinium ILs showed low toxicity to all bacteria strains and freshwater green algae screened against. All eight pyridinium and imidazolium ILs showed low toxicity to Gram-positive and Gram-negative bacteria strains tested against, with a significant range in IC_{50} values. However they were 10^3–10^7 higher (less toxic) than other C14–C18 ILs previously reported. Subsequently, a further series of 10 ILs were synthesised directly from mandelic acid and were evaluated for their antimicrobial toxicity and also their biodegradability in the Closed Bottle Test.

References:

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2 Ghavre, M.; Byrne, O.; Altes, L.; Surolia, P. K.; Špulák, M.; Quilty, B.; Thampi, K. R. and Gathergood, N., Green Chem., 2014, 16, 2252.
3 Ventura, S. P. M.; Gurbisz, M.; Ghavre, M.; Ferreira, F.M. M.; Gonçalves, F.; Beadham, I.; Quilty, B.; Coutinho, J. A. P. and Gathergood, N., *ACS Sustainable Chemistry & Engineering*, **2013**, 4, 393.

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Marine organisms as a source of bioactive metabolites

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[2]*Marine Natural Products Chemistry Research Unit, GEOMAR Helmholtz Centre for Ocean Research Kiel, Am Kiel-Kanal 44, Kiel 24106, Germany*

[3]*Department of Chemistry and Center for Drug Discovery and Innovation, University of South Florida, Tampa, FL 33620, USA*

Abstract:

Oceans cover 70% of the Earth's surface therefore many studies have been conducted on marine natural products over the last decades. Cytarabine and vidarabine were the first marine-derived drugs approved by the FDA in 1969 and 1976 respectively and since then four more synthetic analogues of marine natural products made it to the market.[1] Although thousands of compounds have been isolated from marine macro-organisms, such as sponges, corals and tunicates, research studies have recently turned to marine microorganisms due to the difficulty of re-supply of adequate amounts of the bioactive substance isolated from macro-organisms. Moreover, research groups are interested in marine natural products from an ecological point of view.[2]

This PhD is focusing on the isolation and structure elucidation of secondary metabolites from marine macro- and micro-organisms with both potential biological activities and ecological roles in the marine ecosystem. Therefore our research is targeting bioactive secondary metabolites produced by marine endosymbiotic and endophytic microorganisms like bacteria, fungi, actinomycetes and myxobacteria. Moreover, our studies are focusing on marine natural products from an ecological point of view particularly on the isolation of chemical compounds from Irish algal samples and from marine molluscs, associated with algae. The aim of this research project is not only the isolation and structural elucidation of secondary metabolites with potential biological activity but also the comparison of the compounds isolated from the two different marine organisms. The ultimate goal of this project is to understand the source, function and importance of the chemical compounds that mediate interactions between the two marine organisms. For example, antifungal terpenoid glycoside was obtained through bioassay-guided isolation from a deep-sea holothurian, *Benthogone rosea*. The organism was collected at a depth of 1579 m in Whittard Canyon, NE Atlantic Ocean. It was selected for further chemical work-up due to *in vitro* biological activities of its crude extract, which included antifungal properties against *Candida albicans* and *Cladosporium cucumerinum*, antibacterial activity against *Vibrio fisheri* and cytotoxicity against breast cancer cell line MDA-MB-231. Antifungal activity against *C. albicans* was selected for monitoring the bioassay-guided fractionation of the crude extract. The extract was partitioned in organic solvents and the bioactive aqueous sub-extract was submitted to subsequent reverse-phase High Performance Liquid Chromatography (HPLC) to yield a pure bioactive triterpene glycoside. The structure of the aglycone was elucidated using ^{1}H, ^{13}C, gCOSY, gHSQC, gHMBC, gTOCSY and ROSEY Nuclear Magnetic Resonance (NMR) spectroscopy. Moreover, the sugar moieties are currently being analyzed by hydrolysis, derivatization and will be identified by GC-EIMS spectroscopy.

References:

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2 Puglisi, P.M.; Sneed, M. J.; Sharp, H.K.; Ritson-Williams, R. and Paul, J.V. *Natural Product Reports*, **2014**, 31, 1510.

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Off to On Switching Cellular Uptake Responsive NIR Fluorescent Nanoparticles

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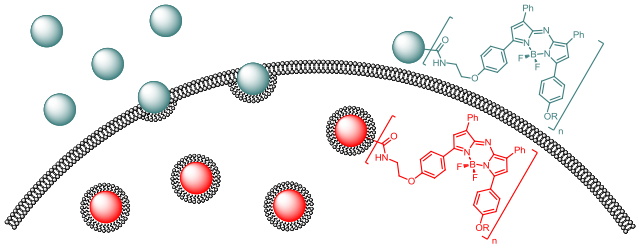

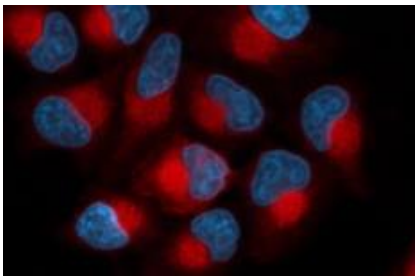

Abstract:

Fluorescence imaging, utilizing molecular fluorophores, often acts as a central tool for the investigation of fundamental biological processes. It also offers huge future potential for human imaging coupled to therapeutic procedures such as fluorescence guided surgery. While several new classes of near infrared red (NIR) probes are currently emerging the opportunity exists to develop a superseding next generation of smart fluorescent probes which have both the optimal photophysical characteristics in addition to the ability of switching their fluorescence signal from *off* to *on* in response to specific biological stimuli. My PhD research concerns synthesis and *in vitro* testing of nanoparticle/NIR fluorophore constructs which are capable of switching fluorescence on following cellular uptake but remains switched off in extracellular environments (Figure). This permits continuous real-time imaging of the uptake process as extracellular particles are non-fluorescent.[1]

References:

1 Palma, A.; Alvarez, L. A.; Sholz, D.; Frimannsson, D. O.; Grossi, M.; Quinn, S. J.; O'Shea, D. F. *J. Am. Chem. Soc*. **2011**, 133(49), 19618

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Session B4
JH3
10.00 am – 12.35 pm

Oral Presentations

Nano-Assembly of Molecular Spin Switches

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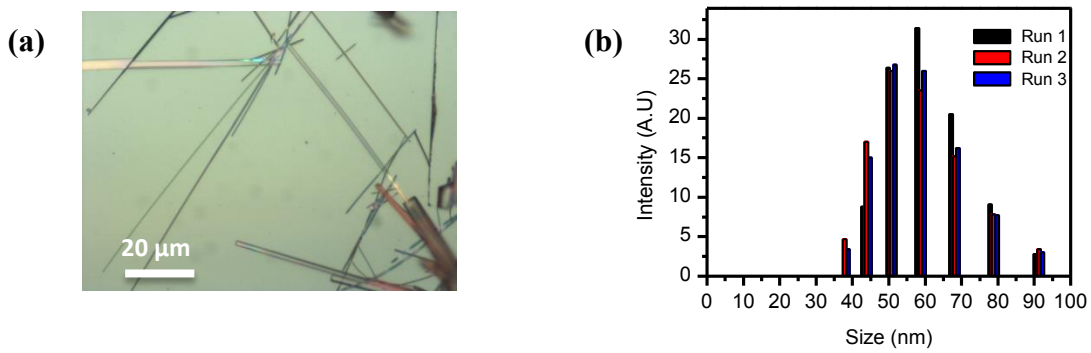

Figure 1. Nanoassembly of Mn(III) (a) Optical images of nanocrystals at 100 x (b) Dynamic light scattering measurements for nanoparticles in water.

Abstract:

Functional molecular switches have gained considerable interest for their potential technological applications. As a result the miniaturization of these functional molecular materials has been explored to determine if there is any change to their physical properties at the nanoscale. Spin crossover (SCO) compounds have been identified as possible candidates for active components in working memory devices due to their capability to stabilize two distinct electronic states, a high spin and low spin configuration.[1] These states are switchable in response to external stimuli such as temperature, pressure or light. SCO compounds can be found among a select group of $3d^4$–$3d^7$ octahedral transition metal ions, the most prevalent being Fe(II), Fe(III) and Co(II) complexes.

The dimensional reduction of SCO complexes has been observed to have an effect on the magnetic behaviour of the materials.[2] This is a result of the electronic bistability being related to the collective behaviour of the SCO centres in the crystalline lattice. We have shown that the SCO properties were retained for Fe(III) SCO complexes.[3] Here, we now probe magnetic, electrostatic and conductive properties of rare SCO Mn(III) complexes at the nanoscale. The successful preparation of a series of nanoassemblies was achieved with Mn(III) SCO complexes, including nanoparticles, nanowires, nanofibers and nanocrystals some of which as seen in Figure 1.

References:

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2. Forestier, T., Kaiba, A., Pechev, S., Denux, D., Guionneau, P., Etrillard, C., Daro, N., Freysz, E., Létard, J. F. *Chem. Eur. J.* **2009**, 15, 6122.
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Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for In-Situ Analysis of Co-Electrolysis

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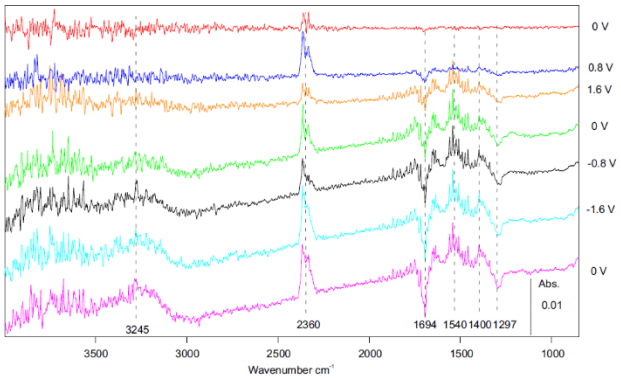

Figure 1. Spectra obtained for a symmetric Au|10Sc1CeSZ|Au Solid Oxide Cell (SOC) in a 5 % CO in Ar atmosphere under D.C. polarization at 600 °C. [1]

Abstract:

Co-electrolysis of carbon dioxide and steam has been shown to be an efficient way to produce syngas[1], however further optimisation requires detailed understanding of the complex reactions, transport processes and degradation mechanisms occurring in the SOC during operation. Whilst electrochemical measurements are currently conducted *in-situ*, many analytical techniques can only be used *ex-situ* and may even be destructive to the cell (e.g. SEM imaging of microstructure). In order to fully understand and characterise co-electrolysis, *in-situ* monitoring of the reactants, products and SOC is necessary.

As part of the UK wide £5.7m 4CU project, we are developing a suite of *in-situ* analytical techniques for high temperature SOC operation. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is ideal for *in-situ* monitoring of co-electrolysis as both gaseous and adsorbed CO and CO_2 species can be detected, however it has previously not been used for this purpose.

Figure 1 shows the DRIFTS spectra obtained using a symmetric cell in a Ar/CO atmosphere at 600 ^{o}C with varying applied voltages.

References:

1 Cumming, D.J.; Tumilson, C.; Taylor, S.F.R.; Chansai, S.; Call, A.V.; Jacquemin, J.; Hardacre, C. and Elder, R.H. *Faraday Discuss*, **2015**, Accepted Manuscript. DOI 10.1039/C5FD00030K

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Chemotactic and Electrotactic Self-Propelled Ionic Liquid Droplets

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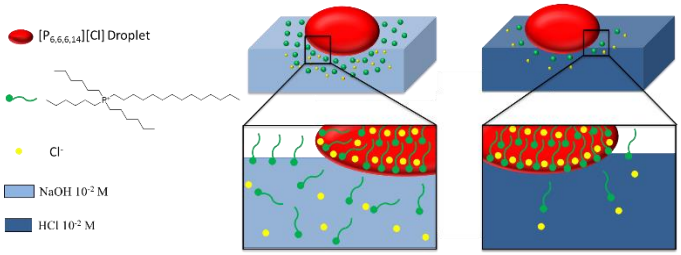
[1]*Insight Centre for Data Analytics, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin, Ireland*
[2]*Australian Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, Wollongong, Australia*



Abstract:

Herein we report the chemotactic and electrotactic self-propelled movement of droplets composed solely of an ionic liquid (IL), namely trihexyl(tetradecyl)phosphonium chloride ($[P_{6,6,6,14}][Cl]$). These IL droplets move spontaneously across the liquid/air interface and are guided to specific destinations within fluidic systems along Cl^- concentration gradients. The self-propelled movement of the droplet is due to the controlled release of the $[P_{6,6,6,14}]^+$, a very efficient cationic surfactant, which is a constituent of the IL droplet. The rate of $[P_{6,6,6,14}]^+$ release depends on the solubility of the closely associated Cl^- anion in the surrounding media, as the formation of free $[P_{6,6,6,14}]^+$ in the aqueous phase depends on the local Cl^- concentration at the IL-aqueous boundary. Therefore, in Cl^- gradients there is an unsymmetrical release of surfactant into the solution, which in turn results in a surface tension gradient around the droplet. This leads to Marangoni like flows which propel the droplet from areas of low surface tension to high surface tension[1].

The required gradients for movement are generated both chemically, by introducing a Cl^- source in the system (*e.g.* HCl, NaCl) and electro-chemically, through redistribution of ions after application of an electric field. Chemically generated gradients quickly come to equilibrium and therefore the droplet will cease to move unless more chemoattractant (source of Cl^-) is added. In contrast, electro-chemically generated gradients have increased lifespan and allow for on demand, multi-directional, reversible droplet movement.

This type of triggered surfactant release provides a compelling mechanism for controlling droplet movement within microfluidic devices, and could form the basis of providing sophisticated functions such as detection of chemoattractant sources, status-diagnosis and auto detection/repair of damage.

References:

1 Francis, W.; Fay, C.; Florea, L. and Diamond, D. *Chem. Commun*, 2015, 51, 2342.

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Closing Keynote Lecture
JH2

Breaking Bad – Fixing Good: Chemistry in Control

Malachy McCann
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Abstract:

In this talk the chemistry in the popular TV series, Breaking Bad, is unveiled. School chemistry teacher Walter White (alias Heisenberg) and his former student, Jesse Pinkman, are spotlighted cooking crystal meth, dissolving a corpse in hydrofluoric acid, detonating mercury fulminate and harnessing the exothermicity of the thermite reaction. The taming of the unstable nitroglycerine molecule to provide explosive sex will also be discussed.

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Poster Presentations

Counterfeit Product Identification using Broadband Acoustic Resonance Dissolution Spectroscopy (BARDS)

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Abstract:

The objective of this work is to demonstrate the potential of a new platform technology called BARDS to discriminate between genuine and counterfeit products, e.g., Cialis, Levitra and Viagra tablets. A simple dissolution test, taking <3 minutes, is shown to provide reproducible changes in the compressibility of the solvent which is unique to a particular tablet formulation. The changes in compressibility are measured through corresponding changes in acoustic resonant frequencies of the dissolution vessel. Counterfeit formulations are shown to produce significantly different acoustic profiles compared to genuine products.

Authentic and counterfeit tablets of the products were measured in duplicate as received using a BARDS spectrometer. A dissolution vessel containing 25 mL of 0.1M HCl was induced to resonate using a magnetic stir bar. Background resonances are observed for 30 seconds before the auto-addition from a tipper of a split tablet. The dissolution medium rapidly dissolves the half tablets which results in outgassing and reproducible changes in the compressibility of the solution which in turn alters the resonant frequencies of the vessel.[1-4] The method harnesses an acoustic effect reported notably by F.S. Crawford.[5]

Time vs frequency plots were obtained during the dissolution of the tablets using dedicated software. Genuine products are shown to yield reproducible and consistent data indicative of formulations produced under high specifications. However, counterfeit tablets produce different acoustic profiles which are less reproducible which indicates poor blend uniformity of the formulations. Different frequency minima in the spectra, as well as the time taken to return to steady state of the system are all indicators as to whether the material being tested is authentic pharmaceuticals or counterfeits when compared to the control of the genuine drug. Further work is required to produce a larger statistical dataset of counterfeit products (n=30).

Broadband Acoustic Resonance Dissolution Spectroscopy was shown to differentiate between genuine and counterfeit samples of three prescription drug products. This represents a rapid 'low tech' approach but with high tech implementation to screen suspect products using genuine product as a reference control.

References:

1. 1 Fitzpatrick, D., J. Krüse, et al. (2012). "**Principles and Applications of Broadband Acoustic Resonance Dissolution Spectroscopy (BARDS): A Sound Approach for the Analysis of Compounds.**" Analytical Chemistry 84(5): 2202-2210.
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5. Crawford, F.S., (1981) '**The hot chocolate effect'** American Journal of Physics, 50(5), 398-404.

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Spin State Ordering and Magneto-optical switching in an Iron(III) Spin Crossover Complex

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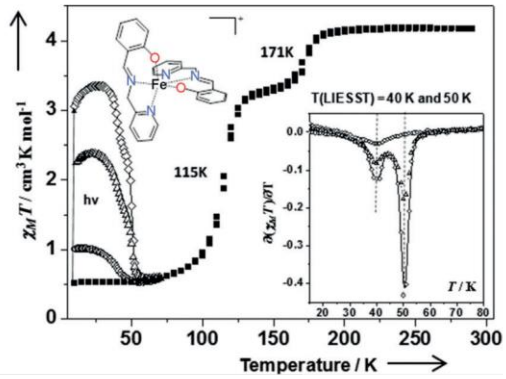

Figure 1. X_mT versus T for (1 ; ▮), showing the LIESST effect on the complex at 10k. Thermal relaxation after (○) irradiation at 647.1nm during 2 h, irradiation at 830 nm during 3 h (△) and 12 h (◇). Structure of the complex cation is shown above the plot. The first derivative in the insert shows a double step relaxation curve. Tranition

Abstract:

The two step spin crossover in mononuclear iron(III) complex [Fe(salpm)2]ClO4·0.5EtO0H (1), is shown to be accompanied by a structural phase transition with spin state ordering on just one of two sublattices in the intermediate magnetic and structural phase.[1] The complex also exhibits Thermal- and Light-Induced Spin State Trapping (LIESST[2] and TIESST[3]) and relaxation from the LIESST and TIESST excited states occurs via the broken symmetry intermediate phase. Two relaxation events are evident in both experiments *i.e.* two T(LIESST) and two T(TIESST) values are recorded. The change in symmetry which accompanies the TIESST effect was followed in real time using single crystal diffraction. After flash freezing at 15 K the crystal was warmed to 40 K at which temperature superstructure reflections were observed to appear and disappear within a 10 000 second time range. Structural and photophysical results from this and related complexes will be presented.

References:

1 Murnaghan, K.D.; Carbonera, C. ; Toupet, L.; Griffin, M.; Dîrtu, M.M.; Desplanches, D.; Garcia, Y.; Collet, E.; Létard, J.-F. and Morgan, G.G. *Chem. Eur. J.* **2014**, 20, 5613.
2 Hauser, A. Top Curr Chem, **2004**, 234, 155.
3 Gütlich,P.; Goodwin,H.A.; *Top Curr Chem*, **2004**, 233, 1-47

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Preparation and Characterisation of Supported Gold Nanoparticles and Application as Radiosensitisers

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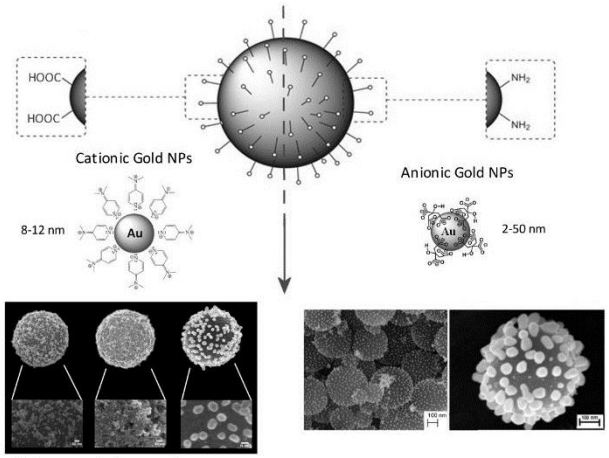
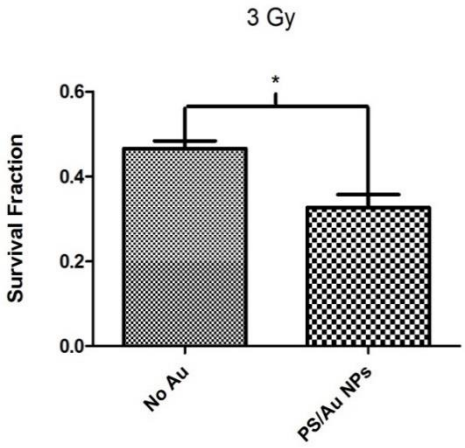
[2]*Queens University, Belfast, Northern Ireland*





Abstract:

Tailored nanoparticle properties have wide ranging potential in areas of energy conversion, catalysis, diagnostics, sensing, imaging and therapeutics.[1] Hybrid materials comprising supported nanoparticles are advantageous as they are easy to handle and manipulate, and also provide a highly localized concentration of nanoparticles.[2] An eloquent example of their application is the use of nanoparticles as radiosensitizers in cells.[3,4] For diagnostic and therapeutic applications the use of a support offers additional avenues for targeted delivery in vivo. Though a variety of methodologies exist to prepare robust composites using gels, polymer networks, micelles, microspheres, achieving a controlled, reproducible and scalable coating remains a key challenge.

The Quinn group is interested in the preparation of supported metal nanoparticles with a high and uniform loading and the application of these hybrid materials as radiosensitizers. In this study the preparation of a variety of composites will be presented together with the methodologies used to quantify the gold loading, as well as the application of these as radiosensitizers with good dose enhancement factors when exposed to radiation.

References:

[1] S. Eustis, M. A. el-Sayed, M. Chem. Soc. Rev. **2006**, 35, 209–217.
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[4] S. Jain et al, *Radiother Oncol*., **2014**, 110, 342-7.

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Asymmetric Grignard Synthesis of Tertiary Alcohols

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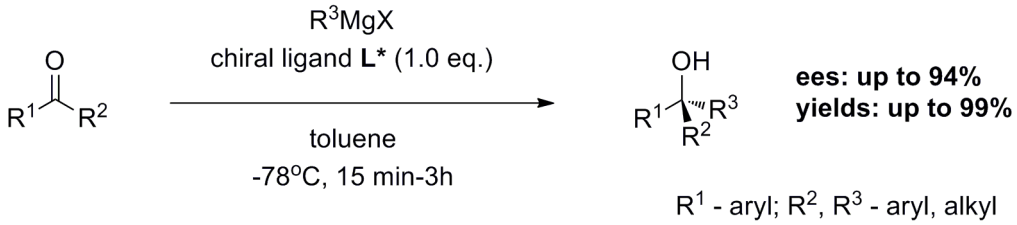

Abstract:

Chiral tertiary alcohols constitute an important class of biologically active molecules.[1] Most conveniently they can be prepared by a stereoselective addition of organometallic reagents to ketones. Among organometallics, the Grignard reagents present the widest scope and greatest versatility. However, stereoselective synthesis of tertiary alcohols by direct 1,2-addition of Grignard reagent to ketones is extremely challenging and most of the successful cases involve transmetallation using transition metals.[2] To best of our knowledge, only a single case was reported to date where high enantioselectivity was obtained in the absence of metals other than magnesium.[3]

We focused our research on development of a general methodology of 1,2-addition of Grignard reagents to arylalkyl ketones in the presence of a new class of chiral ligands. By using stoichiometric amounts of readily available enantiopure ligand **L***[4] it was possible to prepare tertiary alcohol products with high enantioselectivities (up to 94%) and high yields (up to 99%). The method was found to be general for a range of ketones and Grignard reagents. The chiral ligand **L*** can easily be recycled from the crude reaction mixture.

References:

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[3] B. Weber, D. Seebach, *Angew. Chem. Int. Ed.* **1992**, *31*, 84-86
[4] A patent application is pending: upon its projected publication in May 2015 the structure of the ligand **L*** can be revealed.

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Electrochromic Nickel Oxide for Smart Windows

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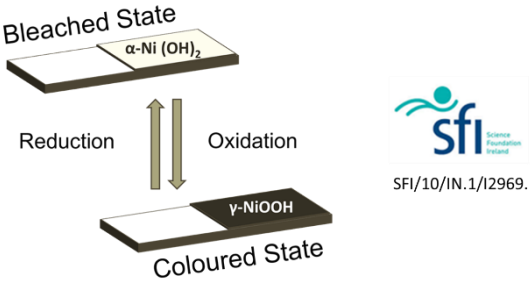

SFI/10/IN.1/I2969.

Figure 2: Bleached and coloured state of NiO_x

Abstract:

Electrochromic materials have the ability to change colour in the presence of an external voltage. This phenomenon is governed by the intercalation and de-intercalation of small ions into and out of the material layers.(1) These materials have potential applications in smart windows and smart devices, due to their low power consumption and high coloration efficiency (CE).(1) The development of this technology may lead to a significant reduction in energy consumption in buildings with a high number of glass windows.

In this study, electrochemically deposited NiO_x films were fabricated under two different sets of parameters.(2) In alkaline media, this oxide can either be transparent (bleached state) or exhibit a dark brown colour (coloured state); depending on the applied potential, Figure 1. In NiO_x, this phenomenon is generally accepted to be governed by the Ni(II) to Ni(III) redox reaction.(2) The electrochromic behaviour of these materials was investigated by Spectroelectrochemistry. Characterisation techniques undertaken on these materials included Raman Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). These results reveal that these materials are a low cost, viable and easily produced alternative to other electrochromic materials currently used in various applications e.g. smart windows and devices.

References:

1. Dhanaji S. Dalavi, Rupesh S. Devan, Raghunath S. Patil, Yuan-Ron Ma, Pramod S. Patil, Materials Letters, 90, 2013, 60-63
2. Muhammad Z. Sialvi, Roger J. Mortimer, Geoffrey D. Wilcox, Asri Mat Teridi, Thomas S. Varley, K. G. Upul Wijayantha, and Caroline A. Kirk, ACS Applied Materials and Interfaces, 5, 2013, 5675-5682.

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Boronic Acid Derivatives for Sugar Sensing

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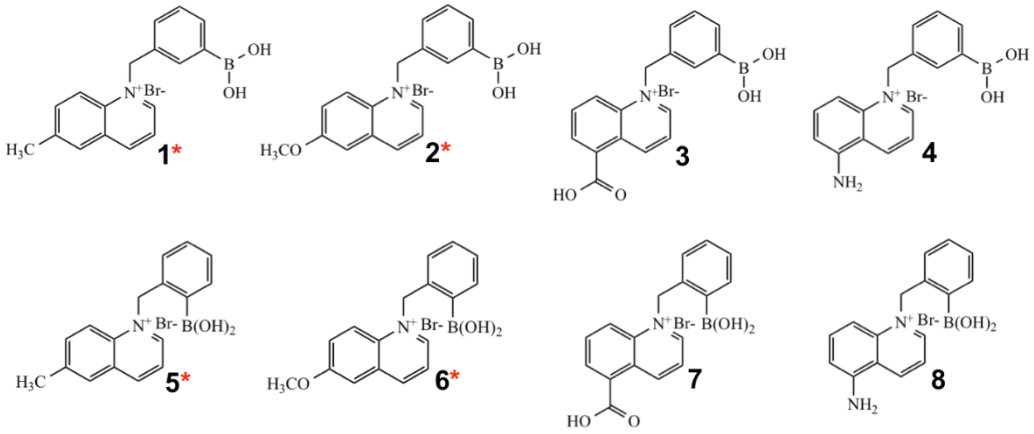

Abstract:

Several boronic acid (BA) derivatives, suitable for sugar sensing (see Figure), have been synthesised *via* a one-step nucleophilic substitution reaction from the appropriate quinoline starting materials and the benzylboronic acid derivative[1]. The quinoline moiety confers the fluorescent behaviour of these sensors through its associated conjugated framework. The BA moiety of the sensor is known for its strong interaction with diols and hence, the sugar sensing application[1,2]. On interacting with sugars (*e.g.* glucose, fructose and lactose) the fluorescence emission decreases with increasing sugar concentration[1]. The BA sensors reported previously in the literature (compounds **1**, **2**, **5** and **6**, see Figure), have been found to be suitable for glucose sensing, in the ocular aqueous humour, in which the glucose range for a healthy person is 300-800 μM, increasing to 200-4000 μM for people with diabetes[1]. As a result, BA sensors have been investigated for glucose sensing when incorporated into platforms, such as smart contact lenses[1,2].

In this present work, novel BA sensors synthesized for the first time by us (compounds **3**, **4**, **7** and **8,** see Figure), will be compared to BA sensor **1** in terms of their fluorescence, sensitivity to sugars and glucose sensing range.

References:

1 Ramachandram, B.: Lakowicz, J.R. and Geddes, C.D. *Journal of Fluorescence*, **2004**, 14(5), 617
2 Ramachandram, B.: Lakowicz, J.R. and Geddes, C.D. *Analyst*, **2004**, 129, 156.

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Exploring the factors which control enantioselectivity in copper mediated C–H insertion reactions of α-diazocarbonyl compounds.

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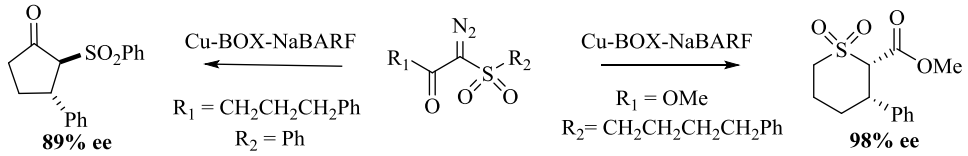
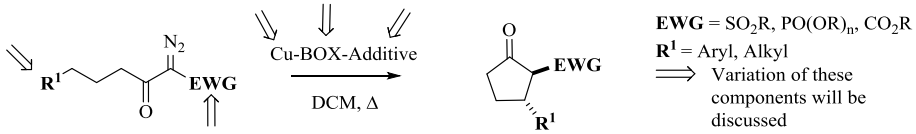
The transition-metal catalysed C–H insertion reaction of α-diazocarbonyl compounds provide a powerful synthetic tool in organic chemistry.[1] The enantioselective cyclisation of α-diazo-β-keto sulfones through asymmetric C–H insertion to form 2-sulfonylcyclopentanones, first reported by McKervey using rhodium catalysts,[2] has been extensively explored in recent years by the Maguire group using copper based catalysts with up to 89%ee.[3]



In related work, enantioselectivities of up to 98% ee have been achieved for the synthesis of *cis*-thiopyrans from α-diazo-β-oxosulfones[4] while up to 82% ee was reported for the synthesis of γ-lactams from α-diazoacetamides.[5] Key to success in the enantioselective C-H insertion is use of the Copper-NaBARF-bisoxazoline catalyst system.[4,6] While the optimal copper source and additive has been identified, the chemo-, regio- and stereo outcomes of the reaction are found to be strongly dependent on the structure of the substrate and the bisoxazoline ligand employed. Our continuing research is focused on investigating the fundamental aspects of the ligand-substrate relationship and how these affect enantiocontrol, with a view to developing new catalysts with broad applicability.

We report herein the outcome of systematic investigation of the impact of variation of each of the structural elements present, namely the substituent R^1 at the site of insertion, the substituent on the carbene carbon (EWG), the nature of the linking chain, the bisoxaline ligand, the counter ion and the additive. Both steric and electronic effects have been investigated to determine the impact of each element on the outcome of the insertion in terms of both degree and direction of enantiocontrol. It is clear from this work that the presence of a sulfonyl substituent on the carbene carbon is particularly effective in leading to high enantiocontrol in these systems.



Research conducted with support from the Irish Research Council.

(1) (a) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861(b) Slattery, C. N.; Ford, A.; Maguire, A. R. *Tetrahedron* **2010**, *66*, 6681.
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Macrocyclic glucuronic acid derivatives: Synthesis and investigation of their potential as anti-tumour agents

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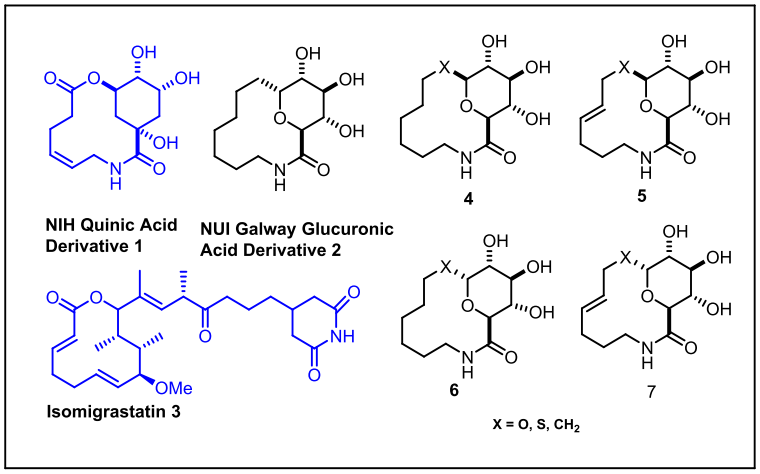

Abstract:

Tumour metastasis is responsible for the majority of cancer deaths and development of inhibitors of this mechanism is considered highly important.[1] Angiogenesis, i.e. blood vessel growth, is an important factor involved in this process. The blood vessels provide the cancerous cells with the necessary nutrients and O_2 required, enabling tumour metastasis.

Preliminary results have shown macrolactam glucuronide **2** is an inhibitor of angiogenesis in an inhibitor of breast tumour cell migration. This compound could be considered to be structurally related to isomigrastatin **3** and quinic acid derivative **1** prepared at the NIH, both of which showed inhibition of tumour cell migration. For this reason a variety of analogues of **2** based on glucuronic acid have been prepared. In some cases chelation induced anomerisation was utilised to generate the macrocyclic compounds with α-configurations at the anomeric centre. These molecules have been prepared for testing as inhibitors of both tumour metastasis and angiogenesis, which will be carried out shortly.

References:

1. Weigelt, B.; Peterse, J. L.; Veer, J. van't;, *Nature Rev. Cancer*, **2005**, 5, 591-602

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Overcoming thermal instability limitations of polymer stationary phases by graphene oxide modification.

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Abstract:

Polymer monoliths in the past have named as the next generation of porous monoliths for applications in separation science. However, typical polymer monoliths exhibit small pore sizes (1-2 µm). Despite lower backpressures than particulate stationary phases, traditional polymer monoliths can encounter blockages when presented with complex biological samples. Polymeric high internal phase emulsions (polyHIPEs) are polymer monoliths fabricated using water in oil emulsions, resulting in a unique pore architecture of voids and interconnecting windows (Figure 1). The typical pore sizes of this class of polymer monolith range from 10 µm to 100 µm, resulting in extremely low operating backpressures and increased flow rates [1].

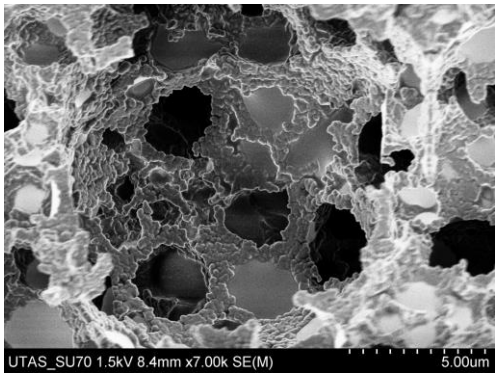

Figure 1. FESEM image of styrene-co-divinylbenzene polyHIPE with 33 pm graphene oxide nanoparticles.

Polymer monoliths are known to have low thermal stabilities of around 200 to 360 °C [2]. In this study to increase thermal stability, styrene-co-divinylbenzene polyHIPE materials were formed within 250 µm I.D. fused silica capillary and were modified with varying concentrations of graphene oxide nanoparticles (GONPs) of ~420 nm in size (Figure 1). The materials were characterised using FESEM, TGA and HPLC of alkylbenzenes showed that addition of GONPs overcame the thermal stability of the materials without compromising its separation capacity. Highlighting the potential of using GONP modified polyHIPEs as stationary due to having superior thermal properties.

References:

1 Silverstein M.S, *Polymer*, **2014**, (55), 304.
2 Essiz S, Sari B, *Adv. Polym. Tech.*, (2014), 33, 21446.

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Expression and *in silico* modelling of Nitric Oxide Synthase enzymes

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2. *College of Sciences and Health, DIT*
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Abstract:

Nitric Oxide, NO, is a vital signalling molecule and is involved in a diverse range of biological processes including neurogenesis, blood pressure regulation and tumour suppression. NO is produced by Nitric Oxide Synthase (NOS) enzymes from L-arginine [1]. There are three NOS isoforms, inducible (iNOS), endothelial (eNOS) and neuronal (nNOS). Over production of NO by nNOS has been linked with a variety of conditions including Alzheimer's and schizophrenia.[2] The project aims to develop a selective inhibitor of nNOS by combining biological, chemical and *in silico* methods.

A combination of structure based and ligand based design has been utilised to identify compounds that have the potential to act as novel nNOS inhibitors. With structure based design, a homology model of human nNOS was developed using rat nNOS as a template. This model was used to screen large commercial compound databases for potential nNOS inhibitors. The structure based approach was used in tandem with the generation of a pharmacophore, ligand based design, which was also used to screen the commercial compound databases. This approach has yielded an array of promising compounds which may act as novel human nNOS inhibitors.

Some inhibitor candidates, identified by the *in silico* models as hits, have been synthesised, while others have been purchased. These compounds have been tested using recombinantly produced human nNOS and a Griess reagent assay, which measures the levels of nitrites produced from L-arginine and the NOS protein. The nNOS protein has been successfully produced in *E. Coli* and purified *via* Ni-NTA affinity chromatography.

References:

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Conformable conducting materials for epidermal sensing

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Abstract:

The human skin is a remarkable and complex organ and its purpose is to protect the body from microbes, help regulate body temperature, and permit the sensations of touch, heat, and cold. In recent years there have been increasing interest in epidermal sensors/electronics that have been devised to apply directly onto the skin and could be used to monitor an individual's health (e.g. skin pH, hydration, temperature, glucose levels, etc.).

Epidermal electronics requires conducting materials that can conform and flow with the mechanics of skin and also deliver good electrical performance. To achieve this, the choice of materials and processing method is critical and the main aim in stretchable epidermal electronics is to combine a high loading of a hard component that is usually conducting (e.g. ink, carbon nanotubes, fibres, etc.) with the overall mechanics that is dominated by a soft material for flexibility.[1]

This study on epidermal electronic materials concerns a commercial screen-printable silver paste composited with elastomer to faciliate movement with the skin. This silver flake/binder/elastomer formulation is screen-printed onto temporary tattoo paper and applied directly onto the skin. The behaviour of the resulting tatoos has been studied in terms of its stretchability, conformability and conductivity.

These new materials have shown promise for for hydration monitoring where capacitive electrodes were fabricated with these materials. These electrodes could be used to measure the tissue dielectric constant (TDC) of the skin. The TDC is known to be directly related to the water content of the skin. A commercial hydration measurement device (MoistureMeterD, Delfin Tech.) was used for assessing the performance of the new tattoo-based capacitive electrodes for hydration measurements. Preliminary results using a phantom skin model have shown that these materials have the potential to be used to track skin hydration over time.

References:

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Measurement of Spinal Flexion using Wearable Sensors

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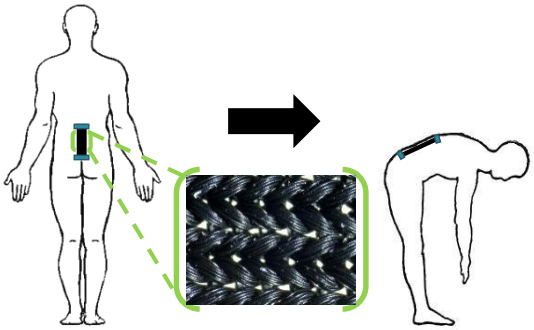

Abstract:

Wearable sensors have the potential to provide new methods of non-invasive physiological measurement in real-time. This work presents an alternative to the current clinical measurement of spinal flexion; the modified Schober's test. The accuracy of the test is determined by each clinician, which causes a large tendency towards error [1]. By implementing a strain sensor as an alternative to the measuring tape currently used, it is proposed that inter-observer error would be reduced and more consistent measurements would be provided over time.

Herein, two types of textile based sensors were tested for use in this application; a knitted spandex cylindrical structure with integrated carbon nanotubes (CNT) and a flat, knitted piezoresistive fabric (KPF) knitted with Lycra® [2]. Of each type, numerous samples were fabricated with varying length, width, core size, tension and knit direction. Each sensor was tested for resistance changes versus strain in the laboratory where it was clear that KPF sensors knit under high tension provided accurate and reproducible electrical properties. All varieties of CNT sensors showed inconsistent resistance measurements over time, rendering them unsuitable for use of such precise measurements. After calibration, it is proposed that these sensors can be easily integrated into a wearable device to be used in a clinical setting.

References:

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2 Pacelli, M.; Caldani, L. and Paradiso, R. *EMBC 2013*, **2013**, 6502.

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Auro-Quant: Design and Fabrication of an Electrochemical Immunosensor (IMMUNO-CAP) for Bovine Progesterone Assessment

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2. Mintek, Nanotechnology Innovation Centre, Johannesburg, South Africa, 2125.

a)

b)

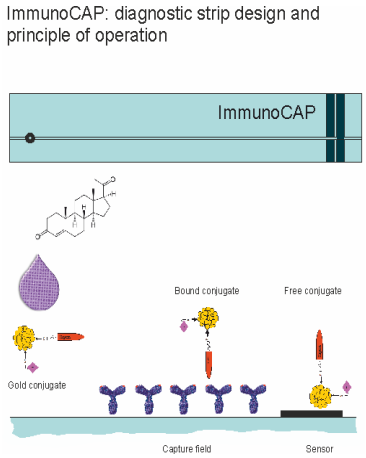

Figure 1. a) Schematic representation of Immuno-CAP, illustrating the structure of a single-channel device and b) showing exploded view of detection mechanism following the competitive immunoassay protocol for progesterone. Device dimensions; 85 x 15 mm (L x W). Channel dimensions; L 74 mm, W 1 mm and D 160 µm

Abstract:

Profitability in the dairy industry is heavily dependent on the accuracy of progesterone (P4) measurement, with periodic assessment of hormone levels in herds being utilised to determine the most fertile ovulation time for artificial insemination. Point of care and in-line instruments, coupling ELISA techniques with electrochemical detection have been explored in order to quantify P4 in bovine milk and serum, yet practical implementation of a sensitive, rapid, low cost test remains a technical challenge. The Immuno-CAP device proposed here may be described as a micro-capillary biosensor incorporating a thin-layer mesofluidic system involving rapid flow immunochromatography with electrochemical detection based on the redox activity of nanogold (AuNP) - the signalling element of a competitive ELISA format. Competition between P4 in the sample and AuNP labelled P4 for binding sites on the internal wall of the anti-P4 antibody coated capillary facilitates electrochemical detection of AuNP reaching the electrode which is in turn related to the free P4 concentration in the milk sample (Fig. 1).

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An autonomous phosphate sensor for remote continuous monitoring.

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Abstract:

There is a growing demand for improved sensing capabilities for phosphorus in water. Phosphorus is a growth limiting nutrient. When levels are elevated, excessive growth of algae occurs, leading to hypoxic or anoxic waters, and the subsequent death of aquatic animals. Real time, continuous monitoring is essential for effective management of nutrient levels in a catchment, by both the detection of pollution events and the identification of point and diffuse pollution sources.[1] Low cost sensors increase capacity for the deployment of sensor networks for diffuse pollution source identification by providing increased spatial data.[2]

A low cost, autonomous sensor with wireless communications has been developed for the detection of phosphate. It is capable of 12 month long deployments. It consists of a waterproof casing, a sample inlet, a filter to remove particles, pumps for fluid manipulation, a microfluidic chip for mixing of water sample and reagents, an LED and photodiode for optical detection, a microcontroller and communications system for wireless communication of data.[2]

A key challenge in terms of nutrient monitoring is the detection limit required. This work shows the optimisation of the autonomous phosphate sensor in terms of sensitivity and the limit of detection. Optimal wet chemistry and a long optical path length enabled improved sensitivity and detection limit.

References:

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2 Buffle, J.; Horvai, G. *In-Situ Monitoring of Aquatic Systems: Chemical Analysis and Speciation*, 6th ed, **2000**.

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Effect of Multi-Walled Carbon Nanotubes on Enzymatic Fuel Cell Anodes

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Abstract:

Enzymatic fuel cells (EFCs) use enzymes as specific catalysts to oxidize glucose at the anode and reduce oxygen at the cathode, converting chemical energy into electrical power. This specificity of enzyme catalysts eliminates the need for casings and ion-exchange membranes, making them a good alternative for traditional metal catalysts in anode and cathode compartments and has led to renewed interest for the development of potentially implantable or portable, miniaturized, membrane-less EFCs operating under moderate ambient conditions and on sugars as fuel. [1-3]

There remain, however, significant issues with the proposed technology, such as low power/current outputs, instability of enzymes and incomplete oxidation of fuels, which have thus investigated a range of studies to improve the performance of EFCs. [4–6]

Addition of multi-walled carbon nanotubes (MWCNT) to the enzyme electrode preparation step results in increased surface area, improved operational output and stability under pseudo physiological conditions. [8–10] These nanostructures provide a support which acts as a scaffold for improved retention of enzymes and electron-shuttling mediators [8, 11, 12] as reported on by many research groups in recent years (Tsai et al., 2009; Tran et al., 2011; Zhu et al., 2011; Tasca et al., 2008).

Here we present a comparison of the glucose oxidation response of films prepared using the previously optimized relative amounts of components, whilst exchange/compare MWCNTs with other conductive and non-conductive nano particles in order to investigate if Conductivity of MWCNTs also help in current density increase or not.

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The Encapsulation of Sulphur in Metal-Organic Materials with a *pcu* Topology via Melt Diffusion for Lithium Sulphur Batteries

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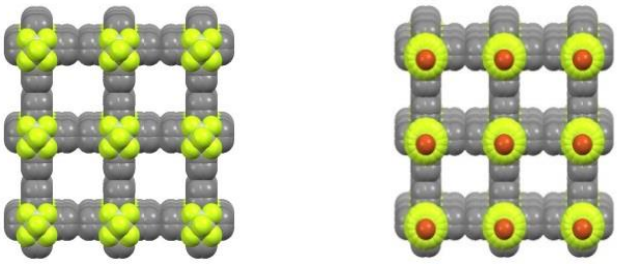

Figure 1: a) *TIFSIX-1-Cu* ($TiF_6(C_{10}H_8N_2)_2Cu)_n$ *and* ***b)*** *SIFSIX-1-Cu* ($SiF_6(C_{10}H_8N_2)_2Cu)_n$ *with 8 Å x 8 Å square channels, viewed along the c-axis*

Abstract:

High energy rechargeable lithium sulphur batteries are regarded as the next generation of batteries due to their high theoretical specific capacity (1675mAh/g). However, this capacity decreases to zero upon the second cycle as a result of the insulating nature of sulphur and lithium polysulphide ions. To address this researchers have trapped the sulphur and lithium polysulphide ions in a porous matrix. Recently, metal-organic materials (MOMs) have emerged as potential candidates for sulphur encapsulation due to their high level of porosity, stability and modularity[1].

Here, we report the encapsulation of sulphur within MOMs with a **pcu** topology via melt diffusion[2]. **Pcu** MOMs, TIFSIX-1-Cu $(C_{20}H_{16}CuF_6N_4Ti)_n$[3] and SIFSIX-1-Cu $(C_{20}H_{16}CuF_6N_4Si)_n$[4], consist of primitive cubic channels arranged in a 3D network with micro-sized 8Å pores, (Fig 1a and 1b). They are good candidates as sulphur cathode host materials due to their pore sizes which are small enough to successfully trap the sulphur and lithium polysulphide ions. They are also large enough to accommodate the lithium ions reaching with sulphur. The presence of the Copper metal at the pore edges encourages the sulphur to bind to the pores more effectively.

Through SEM, PXRD, TGA and BET surface area analysis the presence of sulphur within the MOM was confirmed.

References:

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The effect of glutaraldehyde on the sensitivity and stability of glutamate oxidase biosensors

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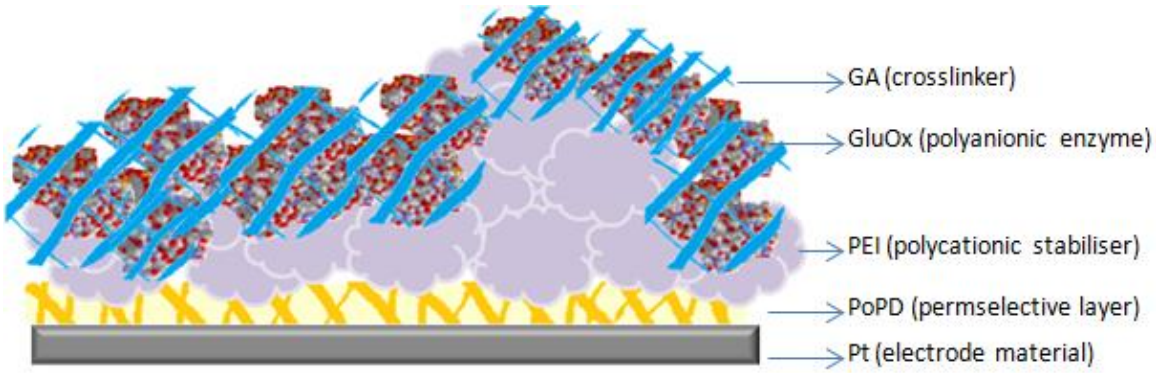

Figure 3: Schematic representation of our typical biosensor design, showing the electrodeposited poly-*ortho*-phenylenediamine (PoPD) on the Pt electrode (1 mm long, 125 µm diameter cylinder), the immobilisation of glutamate oxidase (GluOx 140 kDa, polyanionic) over polyethyleneimine (750 kDa, polycationic), and the crosslinking of glutaraldehyde with the lysine residues located on the glutamate oxidase molecules.

Abstract:

Research into biosensor design for the excitatory amino acid L-glutamate (Glu) is currently a significant area of study due to the important role Glu plays as a neurotransmitter. It is the most widespread excitatory neurotransmitter in the mammalian brain, and has been implicated in a number of neurological disorders such as schizophrenia and stroke. A biosensor is described as an analytical device that contains a biological element such as an enzyme (glutamate oxidase (GluOx) was used here) which is connected to a transducer such as an electrode (Pt here). The enzyme is necessary because Glu is an electro-inactive molecule and undergoes reactions with GluOx to produce electro-active hydrogen peroxide (HP), which is detected by the electrode, facilitating the indirect monitoring of Glu. In this work, a biosensor was designed for the detection of Glu by exploring various modifications of Pt: polyethyleneimine, an enzyme stabilisation agent, to neutralise the electrostatic charge of the negative GluOx;[1] and poly-*ortho*-phenylenediamine as a selectivity layer to block interference from the ubiquitous interference agent, ascorbic acid. Glutaraldehyde (GA) was used as a protein crosslinker, which forms mesh-like structures when GA crosslinks with the lysine residues which are present on GluOx.[2] The inclusion of GA in the fabrication protocol led to a significant increase in the sensitivity and stability of the Glu biosensor.

References:

1 McMahon C.P. *et al.* ANALYST **2006** 131 (1), 68.
2 Barbosa O. *et al. RSC ADV* **2014**, 4(1), 1583.

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Studies on aminophosphonium salts and dynamic kinetic resolution of aminophosphine oxides

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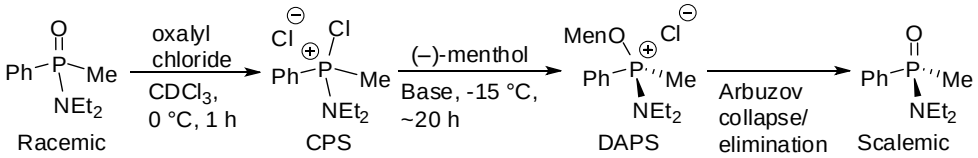
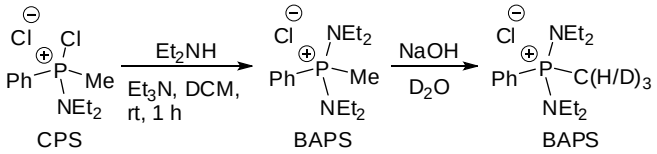
Abstract:

A methodology for the dynamic kinetic resolution of *P*-stereogenic compounds, based on the Appel reaction, has been developed by the Gilheany Research Group [1]. Racemic *P*-stereogenic starting material is converted to rapidly racemising chlorophosphonium salts (CPS) [2]. Reaction of CPS with a chiral auxiliary, (–)-menthol, gives diastereomeric alkoxyphosphonium salts (DAPS), which then undergo Arbuzov collapse to enantioenriched phosphine oxide. The present work applies this method to a new substrate class, phosphinamides, which required elucidation and suppression of competing pathways arising due to susceptibility of P–N bond cleavage *via* HCl.



Scheme 1: Dynamic kinetic resolution of a phosphinamide

Furthermore, an efficient synthetic and purification technique for a bisaminophosphonium salt (BAPS) has been developed which gives quantitative yield *via* high-gradient flash chromatography and exploiting the unique solubility properties of the BAPS. In the presence of hydroxide, aqueous solution of BAPS undergo base-catalysed proton/deuteron exchange, which suggests transient formation of an unstabilised phosphorus ylide.



Scheme 2: Synthesis of a bisaminophosphonium chloride and subsequent proton/deuteron exchange

References:

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Photoresponsive Carbohydrate Azobenzene Conjugates

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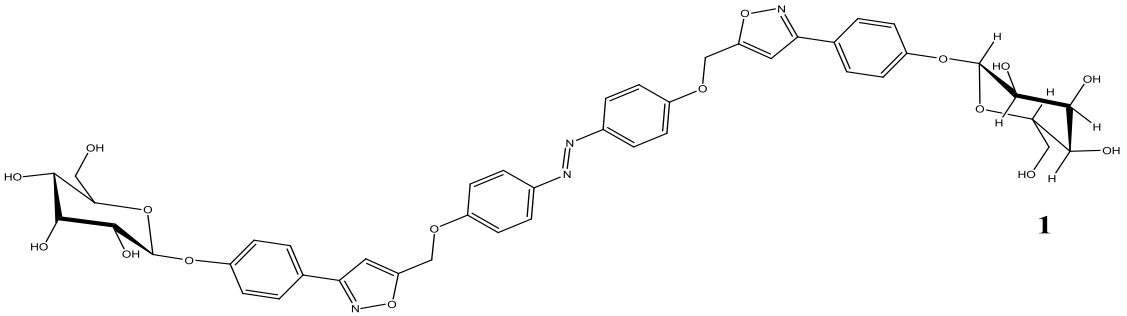

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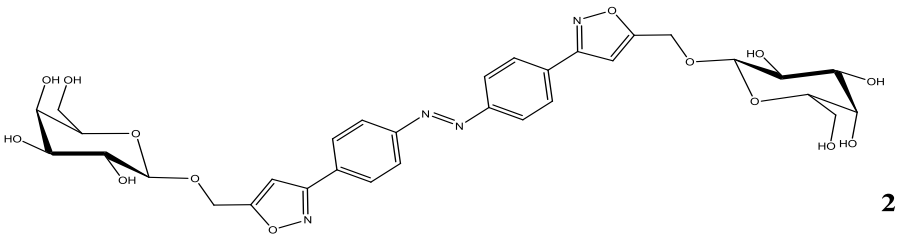

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Abstract:

Azobenzenes have been popular dyes for decades, more recently gaining traction as photoswitches in biological systems.[1] Due to their rapid and efficient reversible switching, biological inertness and significant change in physical properties when switched, they have been incorporated into a range of biologically interesting molecules. As part of our long term goal of developing a robust methodology to bind different classes of biomolecules to an azobenzene core we have focussed on functionalizing the popular photochromic molecule with a range of sugars. A modular approach to these couplings using nitrile oxide alkyne click chemistry has been designed. In this poster we will discuss the formation of conjugates **1** and **2** demonstrating that by attaching either the dipole or the dipolarophile to the carbohydrate unit and the reciprocal functionality to the azobenzene moiety, that azobenzene-sugar conjugates can be created through a 1,3-dipolar cycloaddition.

References:

1 Beharry A.A. and Woolley G.A., *Chem. Soc. Rev*., **2011**, 40, 4422–4437

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Electroactive Bioresorbable Materials for Biomedical Applications

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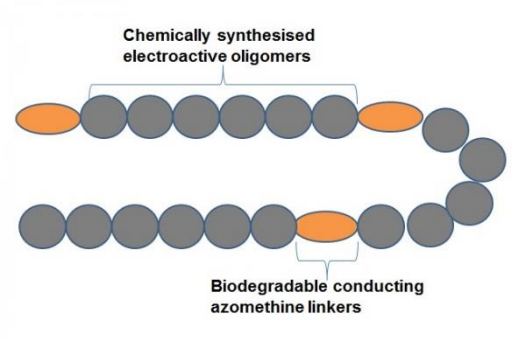

Figure 1: Proposed structure of hybrid electroactive polymer.

Abstract:

During the past decade significant advances have been made in the development of polymeric scaffolds for tissue engineering and drug delivery applications. Typical scaffold materials include co-polymers of lactic and glycolic. While these materials are both biodegradable and bioresorbable, issues associated with the biodegradation process persist including localised lowering of pH by the acidic degrading monomers (lactic acid and glycolic acid). In tandem with developments in organic polymer scaffolds, electro-active conducting polymers have been found to stimulate and promote the growth and differentiation of numerous cell types and as such have been proposed for a variety of applications in the field of tissue engineering.[1] Furthermore, the ability of conducting polymeric materials to facilitate rapid electron transfer and immobilise biomolecules is another distinct advantage advocating the use of these systems in implantable medical devices. Such electro-active materials however, are not intrinsically biodegradable. This major drawback arises primarily due to the alternating π-bond structure required for charge transport. This work focusses on the fabrication of electro-active yet biodegradable/bioresorbable polymeric nanofibres, consisting of both conducting and non-conducting polymeric materials. The dual polymer approach adopts the use of electroactive biodegradable linkers as catalysts for nanofiber degradation thereby providing a platform with significant scope for precise control over degradation rates. In addition the relevancy of this approach to biomaterial design is currently being assessed.

References:

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Structural and Vibrational analysis of Metal Phthalocyanine and Metal Tetraazaporphyrin

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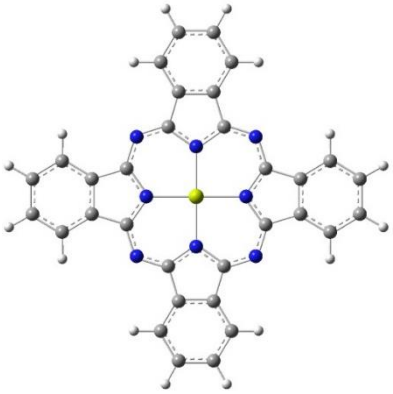
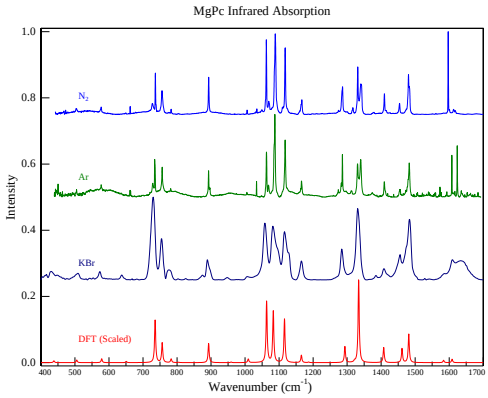


MgPc



Abstract:

A series of metal phthalocyanine (M-Pc) and metal tetraazaporphyrin (M-TAP) systems were investigated using high level density functional theory (DFT) calculations and Matrix-Isolation (MI) spectroscopy. Ground state geometries were predicted by DFT[1]. Two possible arrangements were found to exist; a planar structure exhibiting D_{4h} symmetry (M = Be, Mg, Zn, Al^+), and a non-planar C_{4v} structure (M = Ca, Sr, Ba, Cd, Hg, ClAl) with the metal protruding from the ring. Calculated geometries agree excellently with existing crystal structure data[2]. Group theory allows for a direct correlation of the symmetry blocks of the vibrational modes of the non-planar and planar structures as C_{4v} is a subgroup of D_{4h}. A vibrational analysis has been carried out on MgPc (D_{4h}) and ClAlPc (C_{4v}). Infrared spectra recorded in cryogenic matrices at 12 K as well as in KBr discs were compared with scaled DFT frequencies. Raman spectra recorded in KBr discs using a 532 nm or a 660 nm excitation wavelength were also compared to scaled DFT results. DFT predicts the vibrational spectra of both molecules with excellent accuracy allowing detailed mode assignments to be made. Certain vibrational modes of the non-planar molecules which are optically active in both the IR and Raman in C_{4v} symmetry lose activity upon changing to D_{4h} symmetry. These modes were investigated using DFT calculations and experimental IR and Raman spectra.

References:

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2 R. Kubiak, A. Waśkowska, M. Śledź, A. Jezierski, *Inorganica Chimica Acta*, 2006, **5**, 1344-1350

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Kinetic Modelling of Tautomerisation of Hexose Sugars during Liquid Phase Acid Hydrolysis.

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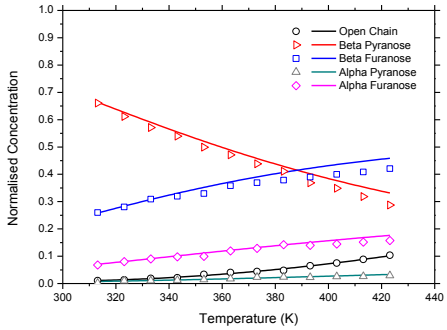

Figure 1. Modelled tautomeric distribution of fructose as a function of temperature in water (lines) based on ^{13}C NMR experimental data by Kimura *et al* [1] (symbols).

Abstract:

The production of 'green' chemicals is vital for the development of a sustainable society and advanced economy. Acid-catalysed hydrolysis of lignocellosic derived sugars has been identified as a key process for the synthesis of platform chemicals such as 5-hydroxy methyl furfural and levulinic acid, whose applications include the production of synthetic fuel components, polymers and more. The reaction mechanism from hexose sugars to 5-hydroxy methyl furfural and levulinic acid is a complex process and fundamental kinetics for such systems is currently beyond state-of-the-art. Yields of 5-hydroxy methyl furfural from glucose, which is the most naturally abundant lignocellosic hexose sugar, have been poor to date. A solution to this problem is promoting the isomerisation of glucose to fructose, which converts more readily to 5-hydroxy methyl furfural. As a result of this, it is necessary to develop robust kinetic models for the hydrolysis of fructose, linking fructose to the lignocellosic derived glucose in a hierarchical manner. As part of the first of step in implementing this plan, this work explores the tautomeric behaviour of fructose and its impact on the reaction mechanism and rates of chemical conversion in an aqueous system with hydrogen cations as intended catalyst. Previous studies using ^{13}C NMR [1] and ^{1}H NMR [2] have identified five main tautomeric species of fructose. This data was used to develop a fundamentally grounded numerical model describing the tautomeric behaviour of fructose. The model was constructed in the temperature window of 283 K and 440 K and was used to postulate and test realistic chemical kinetic mechanisms to describe the conversion of fructose to 5-hydroxy methyl furfural.

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Biodegradation studies of a series of novel L-Phenylalanine derived Ionic Liquids by a modified Closed Bottle Test protocol including targeted synthesis of persistent metabolites

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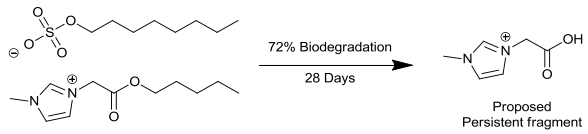
Abstract:

The association of Ionic Liquids (ILs) with green chemistry has increased substantially due to their attractive performance properties such as their solvating abilities, high recyclability, low-volatility, low-flammability, low-toxicity, potential biodegradability and the possibility for their synthesis from renewable resources. However, early generations of ILs such as the butyl-methylimidazolium [bmim] class, have shown to be recalcitrant to biodegradation,[1] calling for the need to examine ILs for biodegradability.

Investigations into biodegradation should help prevent the synthesis of persistent organic pollutants (POP's) - the "**Benign by Design**" concept (Scheme 1). Biodegradation can be measured by a number of prescribed test methods including the Closed Bottle Test (CBT). In this presentation the results of the biodegradation screening of a series of novel L-Phenylalanine derived ILs using a modified CBT protocol[2] will be presented along with analysis, synthesis and structural elucidation of metabolites detected by LC/MS after the test. The ILs synthesised are the culmination of the design lessons learned within the Gathergood and Kümmerer research groups from previous generations of ILs studied. [3-6]



Scheme 1: Readily Biodegradable Imidazolium Octyl Sulphate IL

References:

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Characterisation Techniques for Analysis of Glutaraldehyde Treated Bovine Pericardium

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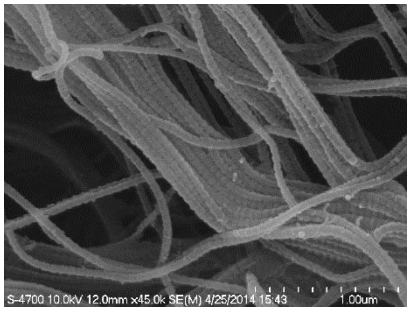

Abstract:

Bovine Pericardium is an extensively used biomaterial with uses varying from vascular grafts to bioprosthetic heart valves. A key reason for the popularity of bovine pericardium is due to its structural components, of Collagen Type I and elastin and its architecture which are responsible for its desirable mechanical properties. Like most biological tissues bovine pericardium is a highly complex structured material. It is non-linear, anisotropic, incompressible and a multi-laminate material [1]. The tissue has to be rendered non-antigenic, immunogenic while still maintaining its mechanical strength properties. This is accomplished through the use of a widely used chemical sterilant organic compound called Glutaraldehyde. It is a 5 carbon di-aldehyde that reacts with the amine groups of lysine residues of the collagen molecules in bovine pericardium. The Glutaraldehyde forms covalent bond crosslinks between inter and intra-collagen fibrils. The treatment reduces biodegradation, antigenicity, increases its biocompatibility, makes it non-thrombogenic and maintains anatomic integrity and strength [2, 3]. Characterisation techniques such as Scanning and Transmission Electron Microscopy (SEM and TEM) can be utilised to get an understanding of the architecture and structure of the tissue while the likes of Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-Red Spectroscopy (FTIR) can give an insight into the degree of crosslinking and the chemistry involved respectively.

References:

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Rational Design and Development of Novel Metal-Based Chemotherapeutic agents

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Abstract:

Metal-based chemotherapeutics are among the most widely used and well known treatments for cancer. Platinum-based metallodrugs such as cisplatin and carboplatin are used in approximately 50% of all cancer treatments worldwide. Their mechanism works by forming adducts with cellular DNA and inducing apoptosis.

Despite the enormous success of platinum drugs, there are drawbacks associated with their use including toxicity and resistance. To overcome these drawbacks, new molecular targets beyond DNA are being actively pursued. Following a multi-targeted approach developed by the Marmion Group,[1-3] we have designed and synthesised innovative metallodrug candidates in which ligands with established anti-cancer properties have been bound to platinum forming potentially novel, multi-functional chemotherapeutics which may overcome some of the drawbacks associated with existing therapies. A summary of our results to date will be presented.

We acknowledge RCSI for providing funding for this research.

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Targeting HSP70 - Development of Bespoke Inert Metal Complexes

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Abstract:

Metal complexes provide an excellent platform for the rational design of drug candidates and the prediction and control of the pharmacodynamics and pharmacokinetics of such compounds. The rational development of metallodrugs that target proteins, though in its infancy, has enormous potential. The metal acting as an inert physiologically stable structural scaffold, can provide improved access to unique 3D diversity space and bind specifically with proteins of interest by inducing selective interactions between bespoke ligand spheres and well-characterised protein binding sites.(1) Ruthenium can be applied due to its octahedral geometry, low toxicity, and well-established synthetic chemistry. (2)

Much research has been undertaken to identify novel biomolecular targets for anti-cancer therapeutic exploitation. HSP70-1 is overexpressed in many cancers and is associated with cancer progression, chemotherapy resistance and poor prognosis as it is thought to provide cancer cells with a survival advantage by conferring protection against apoptosis, influencing senescence and inhibiting autophagy and HSP90 client protein function. (3, 4)

Consequently, we wish to develop inert metal complexes that specifically inhibit HSP70-1 as potential alternative treatments for colorectal cancer that could have intrinsic or acquired resistance. A summary of synthetic chemistry, molecular modelling and molecular biology results to date will be described.

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4 Murphy, M.E. Carcinogen, **2013**, 34 1181.

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Ruthenium-polypyridyl complexes and ruthenium functionalized gold nanoparticles for biological applications

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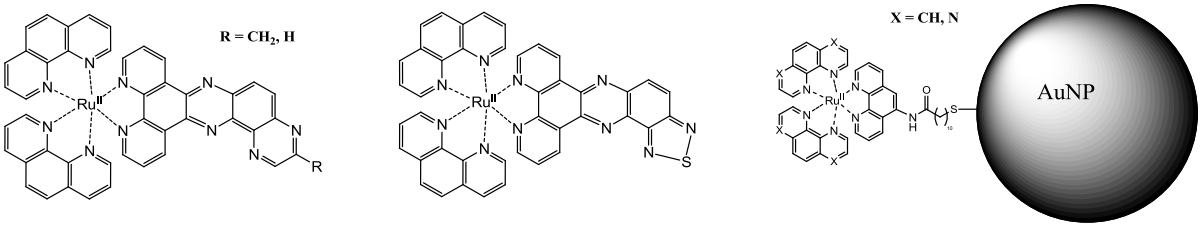

Abstract:

Ruthenium-polypyridyl complexes with extended aromatic ring systems exhibit attractive photophysical properties and have been shown to bind strongly to DNA through intercalation. This makes them suitable for a broad range of biological applications.[1] By focusing on DNA binding we aim to develop novel ruthenium-polypyridyl complexes that can be used as phosphorescent dyes for imaging or as photodynamic therapeutic (PDT) agents in cancer treatment. We have also explored the possibility of functionalize gold nanoparticles with ruthenium-polypyridyl complexes that among others can help with cellular uptake.[2]

Herein we present new ruthenium-polypyridyl complexes. We have evaluated their bindings interactions with DNA by various spectroscopic techniques and all were shown to bind strongly ($K_b > 10^6$ M^{-1}). The potential use as imaging probes has for some of the complexes been demonstrated by a dramatic enhancement in their emission in aqueous environment upon binding to DNA. We have also studied the behaviour of these complexes in HeLa cervical cancer cells, determined their cytotoxicity, and explored their ability to act as luminescent dyes and PDT agents.

References:

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Lewis Acid Catalysed Diels-Alder Activation of α,β-Unsaturated Aldehydes Using Ruthenium (II) Complexes

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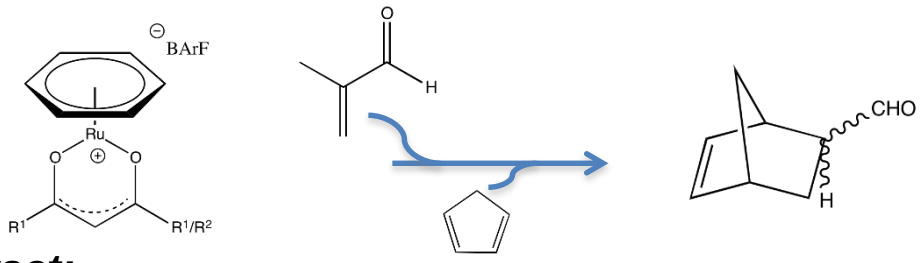

Abstract:

The focus of the Phillips' group is the rational design and synthesis of ruthenium based catalysts, which exhibit moderate oxygen stability, in addition to an increased rate of substrate-product exchange[1]. Such catalysts demonstrate high reactivity in the dehydrogenation of ammonia-borane[2], in particular the β-diketiminato complexes, however, this reactivity is slowed significantly when complexes based on diketone type ligands are employed. It was for this reason that the mechanism in an alternative catalytic reaction was examined.

A range of symmetric and asymmetric η^6-arene ruthenium (II) diketone complexes were prepared and used in the catalytic activation of α,β-unsaturated aldehydes. Normally, these types of complexes are prone to self-dimeristaion *in-situ* affording it more difficult for the reaction to occur at a coordinatively blocked metal centre, thus slowing or even stopping the rate of conversion. It was desirable for these diketones to have bulky substituents, from which a comparison in the reactivity of dimerisation could be made versus less substituted groups.

The reactivity of these complexes was compared in the Lewis acid catalysed Diels-Alder reaction between the dienophiles acrolein, methacrolein and the diene, cyclopentadiene, with high percentage conversions under mild conditions. The selectivity of these catalysts lies toward the endo adduct in the [4+2] cycloaddition of acrolein with cyclopentadiene and the promotion of the exo adduct when using methacrolein.

References:

1 Schreiber, D.F.; Ortin, Y and Muller-Bunz, H and Phillips, A.D. *Organometallics*, **2011**, 30, 5381-5395.
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Novel Dual SOD & CAT mimics: A New Therapeutic Approach?

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Abstract:

Human metabolism generates free radicals and other reactive species such as superoxide radical $O_2^{\bullet-}$, hydroxyl radical $OH^{\bullet}$ and hydrogen peroxide H_2O_2. SOD and CAT enzymes regulate oxidative stress through the dismutation of these damaging species to less harmful compounds. When oxidative stress is excessive and the enzyme defence is overwhelmed, ROS induce cell damage through attack of lipid and protein structures which can lead to disease. Copper(II) complexes with square planar geometry & N_2O_2 binding mode have shown anti-candida[1,2], antibacterial activity[3] and cytoxicity[4,5] on selected cancer cell lines. Previous chemical assays have shown these copper(II) & similar manganese(II) complexes have exhibited superoxide, SOD, and catalase, CAT, mimetic activity[5-9]. Inflammatory conditions such as Alzheimer's, arthritis and tumours are characterised by high levels of ROS, therefore these copper & manganese complexes could provide a novel therapeutic approach as low molecular weight biomimetics. A series of copper(II) complexes containing N_2O_2 donor ligands have been synthesised. Saccharomyces cerevisiae has been used previously as a eukaryotic model to determine the SOD & CAT activity of metal complexes with good results[7,10]. In this research, the model has been optimised for less soluble complexes. Using the BY4741 wild type strain under oxidative stress, this assay has been developed to evaluate the SOD and CAT mimetic activity of these complexes and their protective effect, if any, determined.

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Lanthanide templated self-assembly studies of the versatile 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) ligands giving rise to luminescent materials

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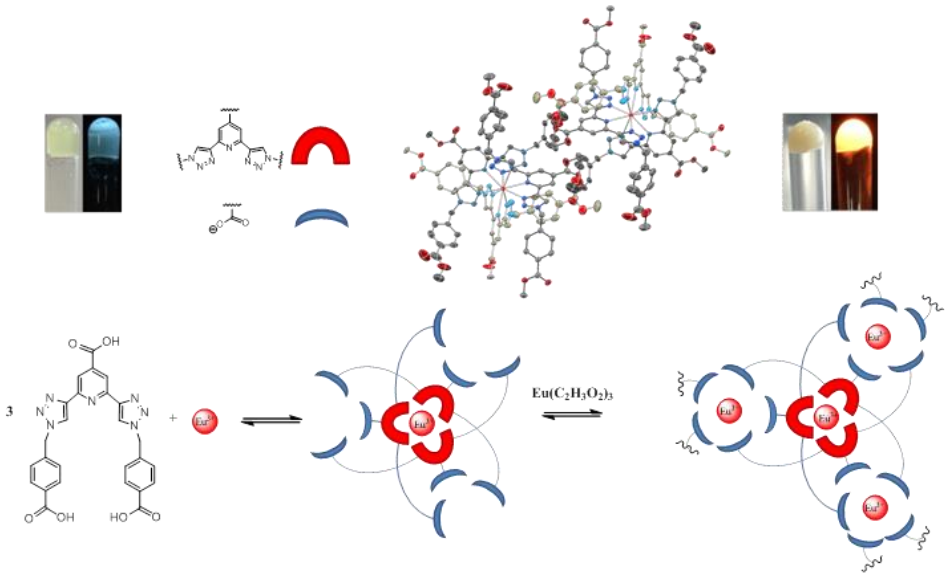

Abstract:

Btp is a member of a family of terdentate pyridine-centred heteroaromatic ligands, which have been shown to form stable coordination complexes with both transition and lanthanide (Ln(III)) metals[1]. In recent times, we have seen that Ln(III) metals have been used to template the formation of self-assembled supramolecular systems.[2] The aim here, to further functionalise the **btp** motif at opening up a whole new library of of substituents as 'handles' to direct the Ln(III) templated self-assembly growth. A crystal structure of the Eu(**btp**)$_3$·[CF_3SO_3]$_3$ was obtained and the self-assembly behaviour upon Eu(III) addition was successfully using non-linear regression analysis. There currently exists a great deal of interest in the search for new materials whose functional properties are different from their monomeric components, thus the tri-carboxylic acid **btp** analogue was synthesised giving rise to the formation of luminescent metallogels.

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Applications of Superhydrophobic Materials

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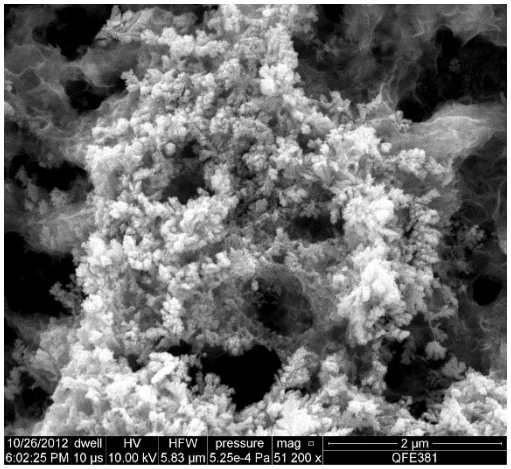

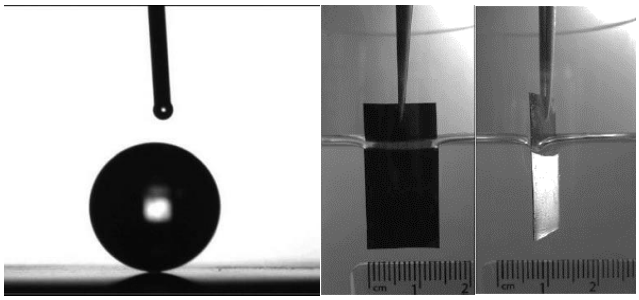

Abstract:

A large amount of research in the area of highly hydrophobic materials has been inspired by examples from nature, for example the lotus plant (*Nelumbo Nucifera*). We have developed a simple method[1] for preparing superhydrophobic (SHP) coatings, based on simple room temperature growth of hierarchical nanostructures followed by chemical modification, which have been widely adopted by fundamental researchers. Here we show examples of how these coatings can dramatically alter the bulk properties of materials and that these can lead to novel functionality.

We have demonstrated that application of a SHP coating to a heat exchange system involving water condensation, such as air-conditioning (AC) units, can dramatically alter the behaviour observed. Since dropwise (rather than filmwise) condensation occurs, the energy consumed by latent heat in vaporising of the condensate droplets means that the electrical power required to produce this output temperature is reduced by up to 20%.

We have also shown how SHP objects exhibit biomimicry in that they possess a plastron when submerged underwater. We demonstrate how a SHP sphere replicates the diving-surfacing behaviour of argonauts (open-ocean pelagic octopuses), and suggest a mechanism for the phenomenon of air-entrapment by diving bell spiders during nest formation.

References:

1 Larmour, I. A.; Bell, S. E. J.; Saunders, G. C. *Agnew. Chem. Ed.* **2007**, 46(10), 1710.

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The Development of Novel HSP70-1 Inhibitor Molecules as Labile Ligands for Pt Anticancer Compounds

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Abstract:

Colorectal cancer is a major cause of death and disease worldwide. Current treatment options depend on the stage of the cancer but can generally include surgery, radiotherapy and chemotherapy. Oxaliplatin, a platinum (Pt)-based compound for example plays a very important and well documented role in treating colorectal cancer [1]. The cytotoxicity of Pt drugs is attributed to multiple mechanisms but primarily their ability to enter cells, hydrolyse and covalently bind DNA, causing the formation of DNA adducts. These events can lead to DNA damage responses and ultimately programmed cell death, apoptosis. The clinical efficacy of Pt drugs is limited however by drawbacks, such as toxicity, but primarily by the high incidence of chemoresistance (intrinsic or acquired) [2]. Since many colorectal cancers are intrinsically resistant to platinum-based therapies there is an urgent need to develop novel and innovative therapeutic strategies for combating colorectal cancer. The HSP70 family of heat shock proteins are highly conserved molecular chaperones whose expression is increased by cells in response to a variety of cellular stresses. HSP70 is overexpressed in colorectal cancer, amongst other cancers, and is associated with cancer progression, chemotherapy resistance and poor prognosis as it is thought to provide cancer cells with a survival advantage [3]. HSP70 is therefore an exciting and legitimate anti-cancer target.
Consequently, we wish to develop novel platinum HSP70 inhibitor complexes as potential treatments for colorectal cancer. A summary of our research to date will be described

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Financial support by Science Foundation Ireland under Grant No.[12/IP/1305] is greatly appreciated.

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Functionally adaptable MBL fold: insights on the alternative role(s) of MIM-1 from *Novospingobium pentaromativorans* and MIM-2 from *Simiduia agarivorans.*

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Abstract:

We recently identified two novel putative metallo-β-lactamases, (Maynooth IMipenemase 1 and 2) [1], from non-pathogenic microorganisms and evaluated their activity towards the three major classes of β-lactam antibiotics [2]. Although both proteins possess β-lactamase activities, comparable to those reported by well-known MBLs from pathogenic bacteria, we were conscious that their *in vivo* activity might be different from β-lactam hydrolysis. For this reason we investigated alternative functions in order to understand the physiological role(s) of the MIMs. We used a database-mining approach to discover related proteins, possessing different activities. Using MIM-1 as a query we discovered two distantly related proteins, the N-acyl homoserine lactonase (AHL) AttM from *Azhorizhobium caulinodans* and the AHL AhlK from *Klebsiella pneumonia* that possess 44% and 43% similarity, respectively. Together with the multiple-sequence alignment, showing the conserved residues shared between the MIMs and the AHLs, we constructed a phylogenetic tree to address common features between the MIMs and AHLs. Since the crystal structures are not available yet, we used a homology modeling approach to generate a model of the putative structures, using AIM-1 as the template. The models built for MIM-1 and MIM-2 are then superimposed to the structures of well-known AHL lactonases and AIM-1 itself, in order to highlight the common features and the differences. In order to further support our finding, we investigated the catalytic activities towards differently substituted AHLs in the presence of the physiologically relevant Zn(II), and other relevant metal ions. Interestingly the plasticity of MIM-1 and MIM-2, already observed in the case of β-lactam antibiotics, is confirmed when AHLs are used as substrates. Although the data reported here are still provisional, they help to outline the linkage between the two subfamilies. Indeed the kinetic data provided support our starting hypothesis, indicating the *in vitro* activity that is comparable with those found in physiologically relevant AHLs. Put together the data that we present, strongly indicate the possible roles of MIM-1 and MIM-2 in the regulation of Quorum Sensing processes in their host organisms.

References:

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Microfluidic Paper Analytical Device for Separations

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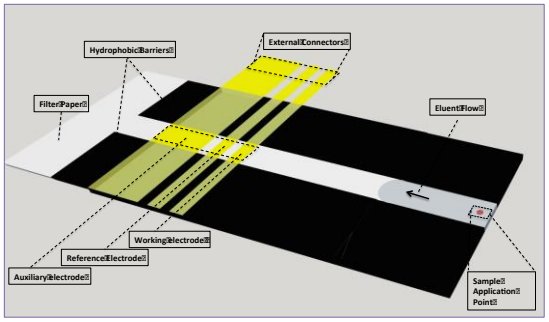

Abstract:

Cellulose-based filter papers were used as base materials to construct microfluidic paper-based analytical devices (µPADs) that coupled a separation channel with electrochemical detection. Channel widths were defined by hydrophobic wax, and gold-sputtering through a mask was used to pattern an electrochemical cell at the end of the channel. Printed channel dimensions were typically 4 mm width x 30 mm length. The physical properties and surface chemistries of various filter papers were studied with respect to the separation and detection of ascorbic acid (AA) and dopamine (DA).

Both the porosity (and hence flow rate) aswell as the ion-exchange capacity of the filter papers were found to influence the separation. Under the conditions used, strong cation exchange filter paper was found to fully retain DA and so was not detected electrochemically at the end of the channel. Standard filter papers, depending on the level of oxidative treatment that they undergo, possess carboxyl groups present on the cellulose fibres that can act as sources of ion-exchange. The capacity of this exchange mechanism was shown to vary dramatically depending on the filter paper used and could be exploited to separate out AA and DA. The µPAD device was shown to be capable of detecting low µM concentrations of DA in the presence of 1 mM AA.

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A Fresh Approach towards the Synthesis of α-Diazocarbonyl Compounds

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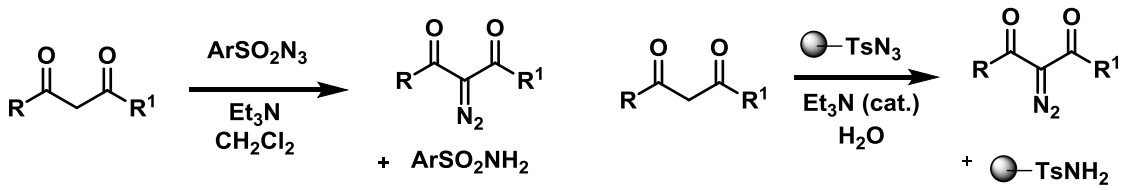

Abstract:

α-Diazocarbonyl compounds play a key role in organic synthesis due to the fact that they are easily prepared, and can undergo a wide range of chemical transformations *via* the initial loss of nitrogen. This is achieved under thermal, photochemical or catalytic conditions and generates reactive intermediates such as carbenes, carbenoids and carbonyl ylides.[1]

There are a number of methods of synthesizing α-diazocarbonyl compounds[2], however the most common method for the introduction of the diazo group is by the methodology developed by Regitz.[3] This involves reacting a substrate such as β-keto esters or β-diketones with tosyl azide in dry acetonitrile using triethylamine or potassium carbonate as a base,[4] however tosyl azide is an extremely dangerous transfer reagent and care must be taken when handling it.[5,6]

Despite their usefulness as intermediates and the range of chemical transformations which they can undergo, these compounds are not routinely used in industrial processes, due to the hazards that are associated with diazo-transfer reagents used such as tosyl azide, and also because they are carried out in harmful and non-environmentally friendly organic solvents such as dichloromethane/acetonitrile. Recently, diazo transfer has been reported in ionic liquids, utilizing sub-stoichiometric quantities of base.[7] With this in mind, we decided to take a fresh look at the synthesis and methodology used to generate α-diazo-β-ketoesters, paying particular attention to doing the reactions in water, using a catalytic amount of base and utilising the safer polymer bound azide as highlighted above.[8] In an extension of this work, using immobilised diazo transfer reagents and catalysts incorporated within a flow chemistry system can lead to these hazards being nullified through safer reactions and cleaner products (environmental aspect), faster reactions, quick reaction optimization and easy scale-up (to produce kilogram quantities).

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Glycosylated Metal Chelators as a Novel Treatment for Alzheimer's Disease

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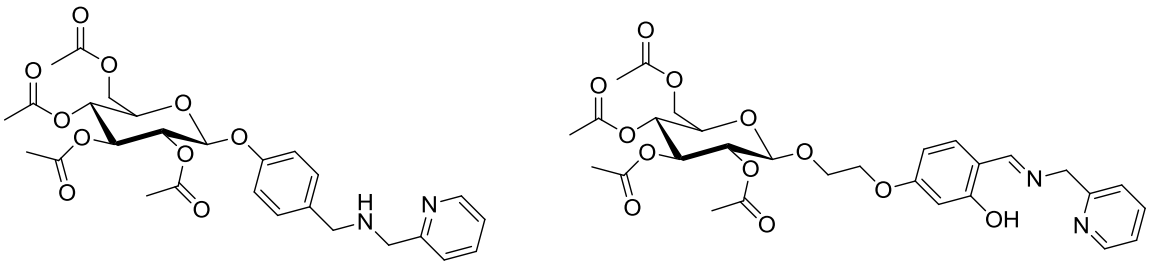

Abstract:

Alzheimer's disease currently affects more than 24 million people worldwide and this number is projected to grow to 81 million by 2040.[1] Current therapies for the disease are limited and the sequestration of metal ions in the brain has been shown to be an attractive target for pharmacological intervention in the disease process.[2]

Carbohydrate conjugated prodrugs are a privileged class of compounds for the treatment of neurological conditions.[3] The use of carbohydrates as a targeting vector allows the drug to cross the Blood Brain Barrier by active transport *via* GLUT receptors.

A library of metal chelators and their glucose conjugated analogues have been synthesised and their ability to sequester iron, zinc and copper ions in solution has been investigated. In addition to this the photochemical behaviour of a family of these compounds has been investigated with the aim of developing a novel reporter system for the monitoring of glycosidase enzymes.

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Molecularly Imprinted Polymers for the capture and detection of biologically active compounds

Alberta Riley, Steven E.J. Bell and Panagiotis Manesiotis

Abstract:

Molecular Imprinting is a technique used for the generation of selective binding sites within the matrix of a synthetic polymer. This is achieved by co-polymerisation of a functional monomer and excess of a cross-linking monomer in the presence of a target substance, the so-called template. During this reaction, binding sites are formed that are complementary in size, shape and functional group orientation to the targeted substance and are capable to selectively recognise and rebind it during application of the material. Such polymers have found extensive use as stationary phases in Solid-Phase Extractions (SPE), chiral HPLC, sensing and catalysis. Target substances include among others pharmaceuticals, drugs of abuse, food contaminants and environmental pollutants.

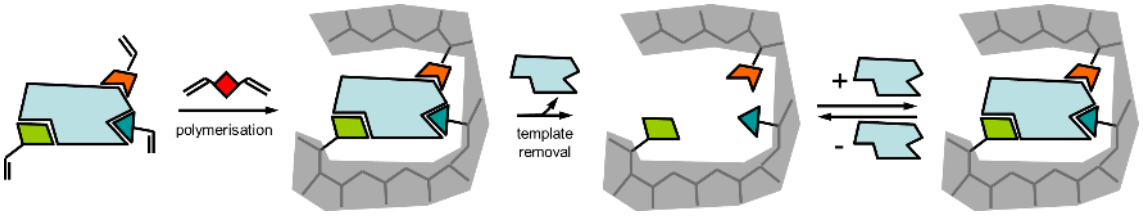

Figure 1: Schematic representation of the molecular imprinting process

Here, we wish to report on the development of materials capable of selective capture of compounds of pharmaceutical and biological interest and their coupling with highly sensitive detection techniques. In particular, we will demonstrate the use of custom made functional monomers on the recognition of drugs of abuse, including recreational drugs or "legal highs", and biomarker nucleoside metabolites, such as adenosine monophosphate (AMP), by stoichiometric imprinting [1].

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Probing the Potential of Nickel and Molybdenum Oxides Nanomaterials for Energy Conversion and Storage

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Abstract:

Finding alternative ways to access and store energy has become a major issue recently. Metal oxides have previously shown promising behaviour as battery electrodes and supercapacitors. In this work we further this research by examining their 2-D counterparts where significant progress has already been made in the field [1]. Bulk MoO_3 and $Ni(OH)_2$ have shown interesting behaviour for energy applications [2, 3], therefore 2-D MoO_3 and $Ni(OH)_2$ have been studied herein. Liquid exfoliation of bulk metal oxides gave access to 2-Dl flakes [4], of different sizes, which exhibit superior electrochemical, charge storage and catalytic activity over the equivalent bulk material , with potential use in the area of energy storage and conversion.

In the present study we examine and evaluate the electrocatalytic behaviour of $Ni(OH)_2$ anode materials for the oxygen evolution reaction in aqueous base and MoO_3 as an anode material for use in the lithium-ion battery system. The charge storage of both systems were studied simultaneously and have been shown to be highly dependent on the sample preparation.

Moreover, physically meaningful equivalent circuit models were determined using electrochemical impedance spectroscopy, which enabled our understanding of the organisation and interfacial behaviour of the surface immobilized nanoflake modified electrode in different potential regimes.

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Silica-based photonic crystals embedded in a chitosan-TEOS matrix: preparation, properties and applications

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Abstract:

Photonic crystals are materials constructed of nanoscale colloidal particles which self-assemble to form an ordered crystal lattice structure. Being on the order of the wavelength of visible light means that various light interactions occur, resulting in the observation of visible colour from the photonic crystal, with the colour observed depending on the diameter of the colloidal particles which form the crystal lattice structure. A key characteristic of a photonic crystal is refractive index (or dielectric constant) contrast[1]. Photonic crystals composed of colloidal SiO_2 particles, as well as other materials are utilized for their interesting optical properties as the regularly repeating crystal lattice interacts with light of different wavelengths depending on the dimensions of the crystal lattice[2]. Successfully introducing colloidal particles into a stimuli-sensitive framework, such as an interpenetrating polymer network (IPN), allows for manipulation of the lattice structure as the crystal lattice would be expected to swell and shrink as the framework reacts to external stimulus. As the crystal lattice swells/ shrinks a shift in the Bragg diffracted wavelength of visible light reacting with the lattice should be observed. IPNs composed of chitosan (Chi) and tetraethylorthosilicate (TEOS) using chitosan sources of varying molecular weight and varying volumes of TEOS were prepared. Analysis of these membranes indicated which type of chitosan gave the best results as a candidate for the formation of a Chi-TEOS-SiO_2 composite and from this an approach for the synthesis of a free-standing Chi-TEOS-SiO_2 composite was investigated.

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Antibacterial and Anti-Cancer Properties of a Silver-Quinone Triangular Clusters

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University College Dublin

Abstract:

In recent years coordination-driven self-assembly of discrete units to miniaturize new supramolecular assemblies and networks has received great interest. These supramolecular assemblies have potential application in molecular electronics[1] catalysis[2] and biology[3]. High nuclearity clusters incorporating with metals with shape defined supramolecular structures such as squares, rectangles, rhomboids, highly symmetric polyhedrons, and triangles[4] are reported. These shape-defined structures are good substrates and often have appealing optical, magnetic or catalytic properties enabling their use in catalysis or optics.

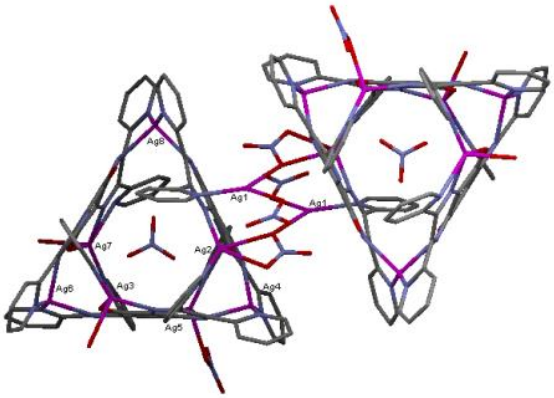

Fig1.1 [Ag(TPTAA)] triangular silver cluster complex

In this work we report the synthesis of a triangular silver cluster using the ligand TPTAA, **L15 fig 1.1**. The novel synthesis of *p*-quinone ligand. TPTAA and its reactivity towards silver(I) is reported. Silver(I) is our ion of choice to synthesize high nuclearity clusters as silver is known to be a medicinally important metal and its reactivity can be enhanced if it is delivered in high concetration.

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The Future is Bright – Applications of Fluorescent Nanographene and Fluoroanthene Derivatives in Material Science

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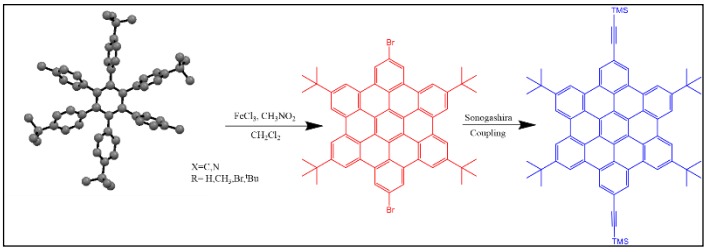
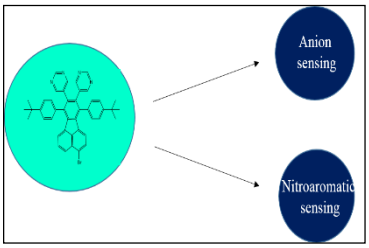
Polycyclic aromatic hydrocarbons (PAHs) show great potential as the active layers in molecular electronics because they possess a desirable set of optical and electronic properties. [1] Incorporating heteroatoms into the periphery of PAH derivatives has a significant influence on these properties. The development of fluorescent chromophores for sensing biologically and environmentally important anions and nitroaromatic compounds has attained significant attention in the field of chemical sensors. [2,3]

In this project, two families of PAHs were synthesized, namely hexabenzocoronenes (HBC's) and N-doped fluoranthene derivatives with differing peripheral functional groups. The former were generated from a series of brominated HBC's and were further converted to trimethylsilyl (TMS) to increase their fluorescence emission which is the key factor for their application as sensors. (Scheme 1a).

A number of photophysical investigations were carried out to determine the nature of the fluorescence. The species were titrated against sources of F^-, Cl^-, Br^-, I^-, ClO_4^-, NO_3^-, HSO_4^- and HPO_4^{2-}. In particular the N-doped fluoranthene derivatives were tested for their ability to detect nitroaromatic compounds in low concentrations. Preliminary studies demonstrated that the HBC derivatives show high sensitivity and specific selectivity over a rapid response time, toward halide anions. This novel class of functionalised PAHs open up new possibilities in developing materials for sensor applications.



1a



1b

Scheme 1: 1a Synthesis of HBC derivatives via the Scholl reaction (intramolecular cyclodehydrogenation) and subsequent Sonogashira coupling. **1b** Molecular structure of a typical N-doped fluoranthene.

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Development of a caffeine sensor for use with in-line monitoring of PAT in the food and beverage industry

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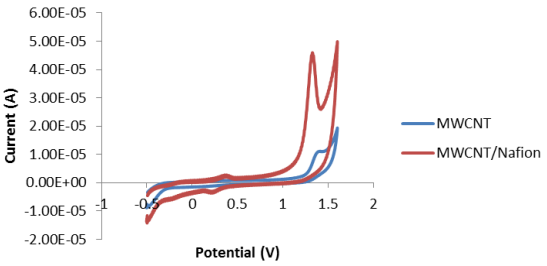

Fig.1. Electrochemical detection of caffeine: comparison of MWCNT-modified (blue) and Nafion/MWCNT-modified (red) GCE.

Abstract:

Food and beverage quality and safety have become of significant importance over the past decade and assuring the highest standards of process control is a key priority. The FDA's Process Analytical Technology initiative emphasises that "quality cannot be tested into products; it should be built in or should be by design" [1]. This has generated a large amount of interest in new technologies for the analysis of pharmaceuticals, food, petroleum and many more. As with the pharmaceutical industry, the food industry faces high regulatory standards regarding the quality control; safety and traceability of their production processes. Advances in modern electronics and data acquisition technology have made it possible to potentially place a wide range of instrumentation at a number of sampling points in many industrial processes. In this work, chemical sensors for the on-line detection of caffeine in real samples have been developed and tested. Two electrode types, a Glassy Carbon Electrode (GCE) and a Screen Printed Carbon Electrode (SPE), were compared for performance. The assay conditions for caffeine detection were then optimised, using Nafion, Multi-walled Carbon Nanotubes (MWCNTs) and a Nafion/MWCNT mixture as electrode surface modifications to explore the possibility of increased electrode sensitivity. The effect of pre-treatment procedures on the performance of the SPE was also investigated. As expected, the MWCNT/Nafion modification showed the greatest improvement in electrode response, when compared to the other modifications. Caffeine was successfully detected in real soft drink samples using both electrodes. The results indicate the potential of electrochemical sensors to compare and compete with the current off-line methods of caffeine analysis, such as HPLC, allowing for both a reduction in time and cost of product quality analysis.

References:

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Electrochemical analysis of Silicon-Coated Germanium Nanowire Heterostructures as advanced Lithium-ion Battery Anodes

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Abstract:

Lithium-ion batteries offer efficient electrochemical energy storage with long cycle life; however they are limited to powering small electronic. Harnessing their potential to power electric vehicles would have major societal and environmental implications due to the current fossil fuel reliance. Realising this requires lithium-ion batteries with superior energy properties and stability. This involves a complete re-evaluation of the battery's electrode materials. Commercial graphite based anodes have a maximum specific capacity of 372 mAh/g. Si and Ge are interesting anode materials due to high theoretical capacities of 4200 mAh/g and 1600 mAh/g respectively. However, their use as anodes is inhibited by a 300% volume expansion during cycling. NWs have been identified as a way to withstand the volume change.

Our group has developed an efficient solvent vapour growth (SVG) system [1] to grow Si and Ge NWs directly from a stainless steel current collector which can be used binder-free in a Li-ion battery. Recently, our group has reported high-performance Li-ion anodes from Ge nanowire arrays which retain capacities of ~900 mAh/g after 1000 cycles[2]. Here we report the cycling data of Si coated Ge NWs. The Ge NWs were synthesised in an SVG system, followed with a post-synthesis Si coating. SEM analysis of the substrates show that high yields of Ge NWs have been evenly coated by amorphous Si (inset Fig. 1). Early cycling data has shown specific capacities greater than 1300 mAh/g for more than 150 cycles (Fig. 1) with promising stability and low capacity fade.

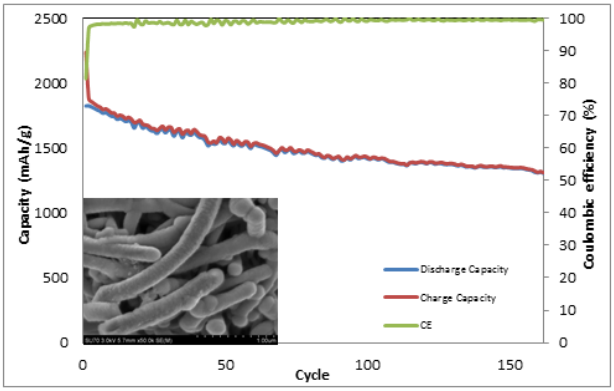

Fig. 1: Charge and Discharge capacities of the Cu seeded Si-coated Ge NW electrode over 150 cycles. SEM image of the Cu seeded Si coated Ge NWs on a stainless steel substrate (inset).

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Development of size controlled chitosan nanoparticles for anti-microbial food packaging applications

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b) Department of Chemistry, University College Cork, Cork, Ireland;
c) Biosystems Engineering, School of Agriculture, Food Science and Veterinary Medicine, Agriculture and Food Science Centre, University College Dublin, Belfield, Dublin 4, Ireland.

Abstract:

Chitosan is a naturally occurring polysaccharide has many unique properties such as biocompatibility, biodegradability and anti-microbial activity [1, 2]. This makes chitosan an ideal food grade anti-microbial. The objectives of this study were to develop a size controlled chitosan nanoparticles (CSNP's) for use as an antimicrobial material.

CS NP's were prepared using an ionic gelation technique, with sodium tripolyphosphate (TPP) as the crosslinking agent. The size and dispersity of the CS NP's were controlled using both an ultrasonic technique and change in concentration of chitosan at initial formation. Antimicrobial properties of the synthesised NPs were assessed using the disk diffusion method and the minimum inhibitory concentration (MIC) was determined using a microdilution method against *Pseudomonas fluorescens* (NCIMB 9046) and *Staphylococcus Aureus* (NCIMB 13062).

It was found that the size and monodispersity of concentrations of 0.5 and 0.75 w/v% CS NPs could be controlled using high intensity sonication; however for 0.1 w/v% CS NPs did not require any external forces to produce monodisperse CS NPs. The anti-microbial assay results indicated that CS NPs of 125 and 250 nm have good anti-microbial properties against both bacterial strains tested. Evidence from the results suggests that monodisperse CS NPs have potential for antimicrobial packaging applications

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Synthesis of Heteroaromatic Lipoxin A_4 Analogues for Biological Evaluation

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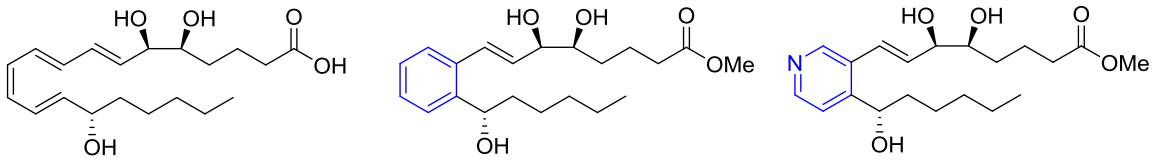
Abstract:

Lipoxins are trihydroxytetraene-containing eicosanoids that are biosynthesised from arachidonic acid by lipoxygenase enzymes and possess potent and selective anti-inflammatory activity. There are two native lipoxins; LXA_4 and LXB_4. These were first isolated from human leukocytes by Serhan and Samuelsson in 1984.[1] They activate the ALX receptor on polymorphonuclear leukocytes (PMNs) and monocytes preventing the migration of neutrophils to sites of inflammation thus acting as stop signals. Due to this anti-inflammatory activity, lipoxins are of interest as potential drug candidates for inflammatory diseases such as asthma, rheumatoid arthritis, atherosclerosis, psoriasis, periodontal disease and cystic fibrosis.[2]

LXA_4 is rapidly metabolised *in vivo* and in an effort to prevent this, recent research has been carried out towards the development of more stable analogues.[3] Substantial work has been carried out by our research group in this area, with the successful synthesis of stable benzene and pyridine analogues.[4,5] These analogues were found to significantly increase phagocytosis of apoptotic PMN's compared to native LXA_4 and to supress key cytokines involved in inflammatory diseases.



Our research group is carrying out an extensive SAR lipoxin programme in an effort to design and develop further analogues with increased potency and stability. This poster will outline the synthesis of some novel heteroaromatic LXA_4 analogues which features a Suzuki-Miyaura cross-coupling and an asymmetric hydrogenation as the key reactions.

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Thermo and Salt Responsive poly(Ionic Liquid)s

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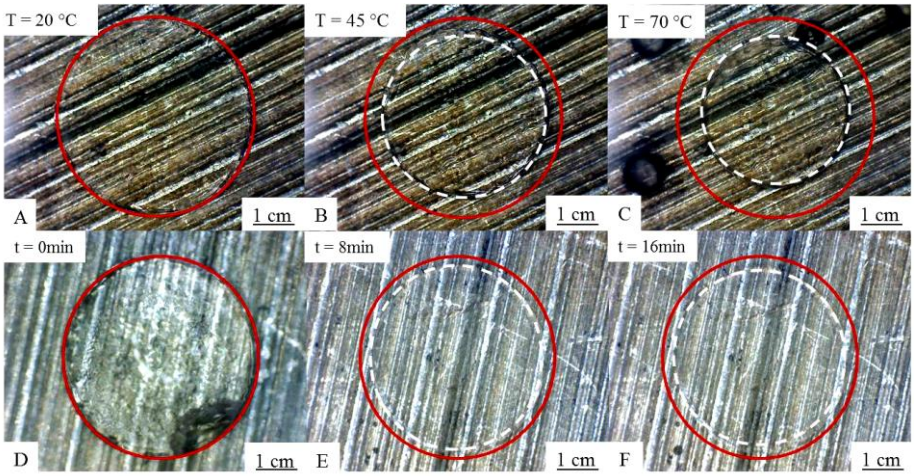

Abstract:

Poly(Ionic Liquid)s (PILs) are a class of ionic liquids that feature polymerizable groups in either the cation, the anion or both. PILs can be used in various applications, including conducting materials for solar cells, lithium-ion rechargeable batteries, and soft polymer actuators [1]. Several PILs show the presence of a lower critical solution temperature, making them suitable precursors for the synthesis of stimuli-responsive materials [2]. The aim of this study was to synthesise PIL hydrogels, namely poly(tributylhexyl phosphonium sulfopropyl acrylate) and characterise their swelling/contracting behaviour under varying temperature and salt solution compositions. For the thermo-response, measurements indicated an average area shrinking of the hydrogel of 53.37% ± 12.55% (N=3) when the temperature was raised from 20 °C to 70 °C (A-C, see Figure). The gel was also found to contract by 17.13% ± 2.29% (N=3) was obtained when the hydration solution was changed from DI water to 1 wt% NaCl solution (D-F, see Figure). This interesting dual-stimuli responsive behaviour will be further explored by forming PIL gel structures within microfluidic chips, and using heat or electrolyte stimuli to change flow rate, flow direction, and disrupt laminar flow in microchannels.

References:

1 J. Yuan, D. Mecerreyes, M. Antonietti, *Prog. Polym. Sci*., 2013, **38**, 1009-1036.
2. S. Gallagher, L. Florea, D. Diamond, *Int. J. Mol. Sci.*, 2014, **15**, 5337-5349.

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Bioinspired antifouling coatings: investigation of surface properties and structural motifs

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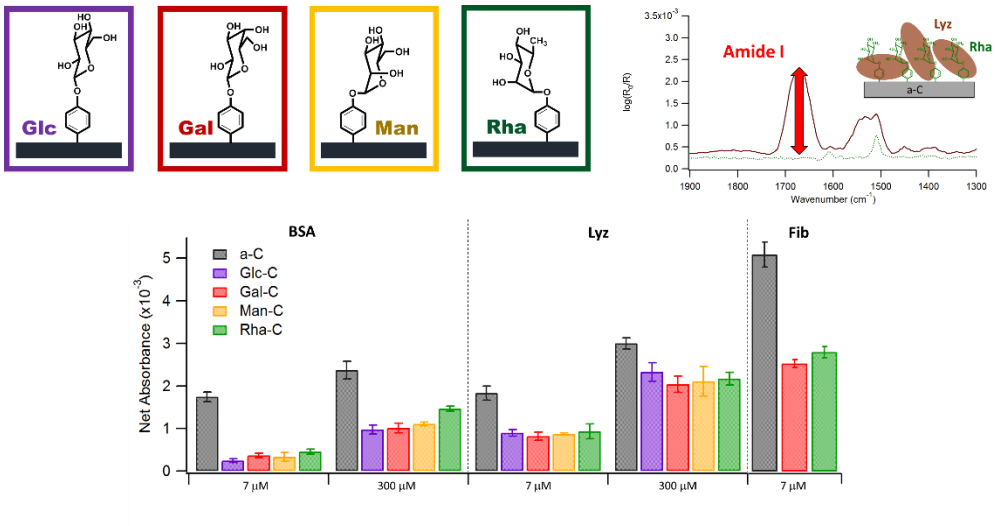

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Abstract:

The glycocalyx found in certain cell membranes consists of an ensemble of glycosylated molecules which direct specific cell-cell interactions and biological recognition events and, furthermore, can inhibit nonspecific adhesion of other cells and molecules at the cell surface. Mimicking the antifouling properties of the glycocalyx offers a promising strategy to prevent clinical problems associated with nonspecific adsorption of plasma proteins on implants and medical devices, such as thrombosis. Saccharide layers or saccharide-decorated molecules have recently emerged as a new class of synthetic antifouling coatings. Surprisingly, even small monosaccharide units appear capable of preventing/minimising protein fouling. Here, we report a study of protein adsorption at carbohydrate-modified and bare amorphous carbon (a-C) surfaces, using a combination of spectroscopic and nanogravimetric methods. The adsorption of three proteins from buffer saline solution was investigated using surfaces coated with four monosaccharides. We show results indicating that the carbohydrate layer significantly reduces surface protein adsorption, particularly in the case of protein concentrations close to physiological values in biologically important fluids (e.g. serum). Surface energy, charge and molecular composition are discussed with the purpose of understanding the implications of our results for the design of carbon surfaces that resist protein fouling in biodevice applications.

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NOTES