School of Chemistry
OÉ Gaillimh
NUI Galway
Scoil na Ceimice

66th Irish Universities Chemistry Research Colloquium

19-20 June 2014

School of Chemistry, NUI Galway

BOOK OF ABSTRACTS

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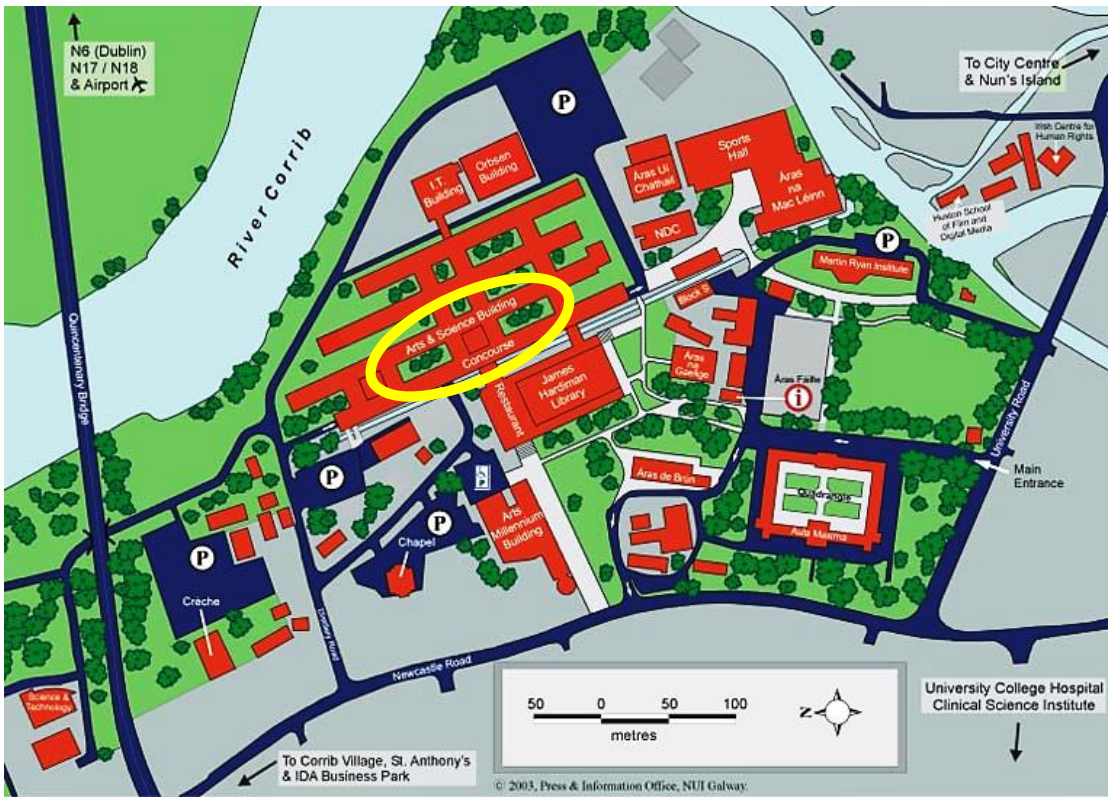
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Civil Engineering
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Education Department
Kirwan Theatre
Dillon Theatre
Larmor Theatre
Tower 1
Library

Thursday, 19th June

Registration (9.30 - 10.30)

Kirwan Lecture Theatre

10.30 **Opening Address**

Plenary Lecture (Chair: P. Murphy)

10.40 **A.F.A. Peacock, University of Birmingham**
De novo designed peptides – Exciting ligands for inorganic chemists

	Dillon Lecture Theatre	Larmor Lecture Theatre
	Session A1 (Chair: A. Erxleben)	**Session B1 (Chair: TBA)**
11.35	**N. Walsh, UCD** *Conjugated polymer nanoparticles for imaging applications: ensemble & single particle photophysics*	**R.B. Driver, NUIM** *Synthesis of novel dienic systems: interesting substrates for asymmetric organocatalysis*
12.00	**P. Liu, UL** *Controlled electrophoresis deposition of aligned films of cadmium chalcogenide nanocrystals*	**N. Mc Cleary, NUIG** *Design, synthesis and catalytic activity of oxazoline based ligands*
12.25	**T.B. Tierney, UL** *Dissolution enhancement by crystal size control*	**D.J. Carr, UCD** *Mechanistic study of the asymmetric oxidation of phosphines under appel conditions: understanding and improving the stereoselection*

Lunch (12.50 - 14.15)

	Session A2 (Chair: A. Kellett)	**Session B2 (Chair: P. O'Leary)**
14.15	**R. Pigot, NUIG** *Rational design of vitamin B_{12}-metal conjugates for the selective delivery of chemotherapeutics into tumor cells*	**K. Manzor, ITT** *Synthesis of a peptide antibiotic derived from a natural food preservative*
14.40	**A. McKeon, RCSI** *HSP70 as a metallodrug target*	**M.-T. Nolan, UCC** *Access to biologically important 2-pyrones via C-H activation strategies*
15.05	**C. Connolly, UCD** *Ruthenium(II)-(BIAN) complexes as DNA metallo-intercalators and exceptionally cytotoxic agents*	**E.C. O'Sullivan, UCC** *From heterocycles to cell cycles: isoellipticines as anti-cancer agents*
15.30	**A. Prisecaru, DCU** *Molecular methods at the metallodrug-DNA interface*	**A. Maginty, QUB** *Non-viral gene delivery vectors: synthesis and in vitro biological evaluation*

Coffee Break & Poster Session (15.55 - 16.40)

	Session A3 (Chair: TBA)	Session B3 (Chair: TBA)
16.40	**D. Branagan, NUIM** *The formation of metal-carbon nanotube composites for applications in non-enzymatic glucose sensing*	**V. Piacenti, RCSI** *Tackling neuroblastoma: design and development of PNA based miR-34a mimics*
17.05	**R. Kumar, NUIG** *Glucose oxidation at enzyme electrodes under physiological conditions for application to biosensors and biofuel cells*	**S. Burrell, DIT** *Stabilisation of paralytic shellfish poisoning toxins in shellfish tissue matrices for the preparation of reference materials*
17.30	**G. Matzeu, DCU** *Non-invasive detection of biological fluids: a new perspective in monitoring pH in saliva and sodium in sweat*	**D. Crowe, ITT** *Computational and NMR based mechanistic studies of L-proline derived organocatalysts*
17.55	**J. Arndt, UCC** *Identifying sources and chemical composition of atmospheric aerosols using single particle mass spectrometry*	

BBQ in The College Bar of NUI Galway (from 19.30 onwards)

Friday, 20th June

	Dillon Lecture Theatre	Larmor Lecture Theatre
	Session A4 (Chair: TBA)	**Session B4 (Chair: L. Ronconi)**
9.15	**Z. Wang, QUB** *Activity and coke formation of nickel and nickel carbide in dry reforming: a deactivation model from density functional theory*	**U. Sheridan, NUIM** *Metal Organic Frameworks based on carboxylate functionalised tetrazole ligands*
9.40	**G. Melia, DIT** *AEROdynamic surfaces through MUltifunctional COatings (AEROMUCO)*	**L.J. Brennan, TCD** *New materials for solar cell applications*
10.05	**A. Serleti, UL** *Design and development of a patterned bio-fuel cell*	**Y. Lu, TCD** *Tapping into the triplet state - New applications and possibilities with 1,10-phenanthroline based Ir(III) and Ru(II) complexes*

10.30 **M. Browne, TCD**
Towards a hydrogen economy: the investigation into the oxygen evolution reaction (OER) using transition metals

A.P. O'Kane, QUB
Extraction of high value products from seaweed for biomedical applications

Coffee Break & Poster Session (10.55 - 11.40)

Kirwan Lecture Theatre

Plenary Lecture (Chair: N. Geraghty)

10.40 **M.J. Hynes, NUIG**
The molecules of murder

12.35 **Concluding Remarks and Awards Ceremony**

TOPICS

Session A1 Nanoparticles/Solid-State Chemistry - Sponsored by *Boston Scientific*

Session B1 Organic Chemistry - Sponsored by *MSD Ireland*

Session A2 Bioinorganic Chemistry - Sponsored by *Janssen Pharmaceutical*

Session B2 Bioorganic Chemistry

Session A3 Analytical Chemistry

Session B3 Organic/Bioorganic Chemistry - Sponsored by *Roche Ireland*.

Session A4 Physical/Computational Chemistry

Session B4 Inorganic/Materials Chemistry

AWARDS

Best Oral Presentation Awards sponsored by *MSD Ireland*.

Best Poster Presentation Awards sponsored by *Roche Ireland*.

PLENARY

De novo designed peptides – Exciting ligands for inorganic chemists

Peacock, A.F.A.*

School of Chemistry, University of Birmingham, Birmingham (UK).

Abstract:

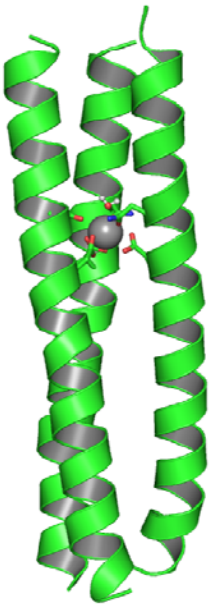

Figure 1. Model of Ln(III) 3-stranded coiled coil.

Our group is interested in coupling small peptides with inorganic chemistry in an effort to develop hybrid systems which couple the advantages of both biology and chemistry.

One project uses coiled coil scaffolds as novel ligands for metal ions. *De novo* designed peptide constructs based on the heptad repeat approach form amphipathic α-helices in solution and above ca. pH 5 these aggregate to form coiled coils. These scaffolds provide a stable framework in the interior of which we can design challenging metal binding sites by incorporating amino acids capable of binding to metal ions. Though significant effort is directed at using these as ligands with which to reproduce biologically relevant complexes, our group is interested in exploiting coiled coils as ligands for metals not in the repertoire of biology. In particular we have developed a range of coiled coils for coordinating lanthanide ions, see Figure. Using these we have demonstrated that despite providing the same first coordination sphere ligand set, the lanthanide coordination chemistry is highly dependent on where this binding site is located within the coiled coil. For example two very similar designs lead to lanthanide coiled coils more suitable for luminescence imaging or for MRI contrast applications, respectively.

A second project is interested in the DNA binding properties of synthetic peptides based on helix-loop-helix motifs, in which the α-helices are linked by artificial domains. Recently we have explored the opportunity to incorporate switching units, which in turn are capable of sequence selectively regulating DNA binding on coordination of metal ions such as copper or zinc.

AFAP gratefully acknowledges financial support from the University of Birmingham. Some equipment used in this research was obtained through Birmingham Science City.

References:

1 Peacock, A.F.A., *Curr. Opin. Chem. Biol.* **2013**, 17, 934.
2 Berwick, M.R.; Lewis, D.J.; Pikramenou, Z.; Jones, A.W.; Cooper, H.J.; Wilkie, J.; Britton, M.M. and Peacock, A.F.A., *J. Am. Chem. Soc.* **2014**, 136, 1166.
3 Oheix, E.; andPeacock, A.F.A., *Chem. Eur. J.* **2014**, 20, 2829.

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SESSION A1

Conjugated polymer nanoparticles for imaging applications: ensemble & single particle photophysics

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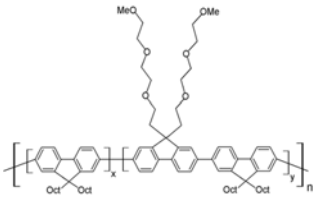

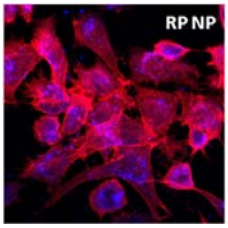

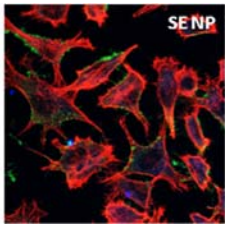

Abstract:

Recent developments in materials synthesis, bio-conjugation methods and luminescence techniques have led to a rapid proliferation of novel fluorescence based approaches to imaging in the life sciences [1]. However, for demanding applications, molecular dyes suffer from limitations such as low brightness, poor photostability and fluorescence intermittency [2]. As a result, there is considerable interest in developing brighter and more photostable fluorescent probes. In this regard, fluorescent conjugated polymer nanoparticles exhibit exceptional brightness and photostability suitable for advanced imaging applications such as super-resolution microscopy and single particle tracking [3]. Consequently, we are exploring nanoparticles of highly fluorescent conjugated polymers that contain covalently grafted oligoethylene glycol side-chains [see figure]. Polymer nanoparticles of different sizes may be prepared – *ca.* 20 nm particles by re-precipitation (RP NP) and *ca.* 90 nm particles by solvent-exchange (SE NP). The particles exhibit high absorption cross-sections (10^{-13}-10^{-12} cm^2), high quantum yields (*ca.* 50%), and size-dependent absorption and fluorescence spectra. Single particle fluorescence imaging studies indicate much higher emission rates (*ca.*10^8 s^{-1}) and little or no blinking as compared with single dye molecules or Q-dots. Analysis of single particle photo-bleaching trajectories indicates excellent photo-stability with *ca.* 10^8 photons emitted per particle prior to irreversible photo-bleaching. Finally, fluorescence microscopy of nanoparticles exposed to L929 and MCF-7 cancer cell lines indicates that the particles are readily internalized by the cells [see figure; actin is red, particles are blue].

References:

1 Saito, K.; Chang, Y.F.; Horikawa, K.; Hatsugai, N.; Higuchi, Y.; Yoshida, Y.; Matsuda, T.; Arai, Y. and Nagai, T., *Nat. Commun.* **2012**, 3, 1.
2 Wu, C. and Chiu, D. T., *Angew. Chem. Int. Ed.* **2013**, 52, 3086.
3 Tian, Z.; Yu, J.; Wang, X.; Groff, L.C. and Grimland, J.L., *J. Phys. Chem. B* **2013**, 117, 4517.

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Controlled electrophoresis deposition of aligned films of cadmium chalcogenide nanocrystals

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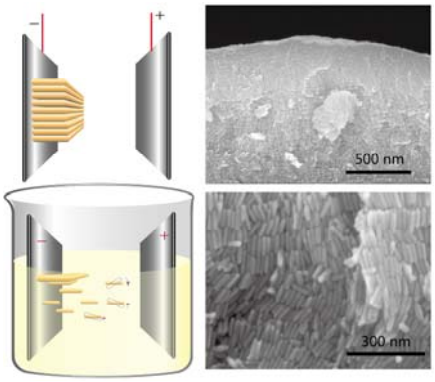

Abstract:

Electrophoresis deposition (EPD) can be used to deposit nanocrystals (NCs) into close-packed films for device fabrications. We overview our recent work on EPD of CdX (Se, S, Se_xS_{1-x}) based NCs from solution, including nanodots (NDs) and length tunable nanorods (NRs). After synthesis, NCs could be charged by partially loss of the capping ligands during purification procedure [1]. Controlled purification of NCs solution effects on the mobility and surface charge (ζ-potential) on NCs. By applying an external direct current (DC) voltage forming an equal electrical field, the NCs were oriented and pushed in the non-polar solvent towards to a substrate placed as electrode. The surface charge have critically influence on the morphology of as-deposited films and the orientation of nanorods [2]. The results shows EPD as an effective and controllable assembly route for depositing colloidal NCs on a wide range of substrates, has remarkable potential to apply in real device processing.

References:

1 Jia, S.; Banerjee, S. and Herman, I.P., *J. Phys. Chem. C* **2008**, 112, 162.
2 Singh, A.; English, N.J. and Ryan, K.M., *J. Phys. Chem. B* **2013**, 117, 1608.

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Dissolution enhancement by crystal size control

Tierney, T.B.*; Rasmuson A.C. and Hudson, S.P.

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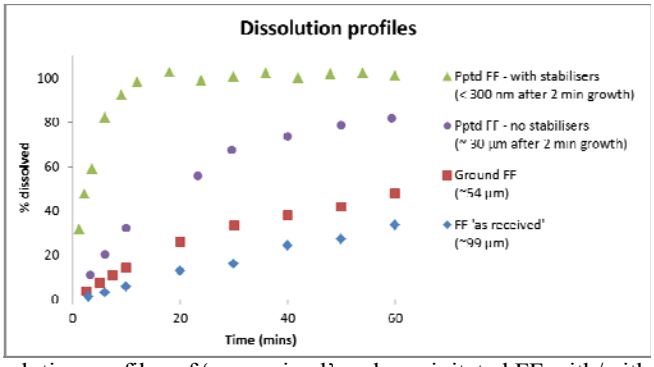

Figure 1. Dissolution profiles of 'as received' and precipitated FF with/without stabilisers.

Abstract:

It is estimated that 40% of promising drug candidates fail to reach commercialization because of their poor water-solubility [1]. Such drugs often present administration difficulties due to poor and inconsistent dissolution properties. The bioavailability of drugs with high permeability and low solubility is limited by their dissolution. One feasible strategy to improve the dissolution properties of such drugs is to decrease their particle size [2]. Controlling the particle size through controlled crystallization eliminates the need for particle size reduction processes such as milling, which is grossly energy inefficient, can introduce impurities and can lead to thermal/mechanical degradation of temperature sensitive materials [3].

Liquid antisolvent precipitation was employed to control the nucleation and growth mechanisms of the hydrophobic drug, fenofibrate. Particle nucleation was promoted by high supersaturation conditions and growth was retarded by use of suitable stabilisers. Particles in the size range 200-300 nm were formed and the nanosuspension was stable at this size for up to 8 minutes using HPMC and SDS stabilisers. To ensure minimum particle size, the precipitated particles were frozen after 2 minutes and isolated by lyophilisation. Dissolution testing of the dried particles showed that the material dissolved approx. 20 times faster than the 'as received' material. Scanning electron microscopy and laser diffraction particle size measurements were used to determine the particle size of both the freshly precipitated and precipitated/freeze-dried particles.

References:

1 Merisko-Liversidge, E.; Liversidge, G.G. and Cooper, E.R., *Eur. J. Pharm. Sci.* **2003**, 18, 113.
2 Hu, J.; Ng, W.K.; Dong, Y.; Shen, S. and Tan, R.B.H., *Int. J. Pharm.* **2011**, 404, 198.
3 Yaeger, S.A., Innovative Milling & Micronization Techniques for the Pharmaceutical Industry, **2008**.

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SESSION B1

Synthesis of novel dienic systems: interesting substrates for asymmetric organocatalysis

Driver, R.B.* and Stephens, J.C.

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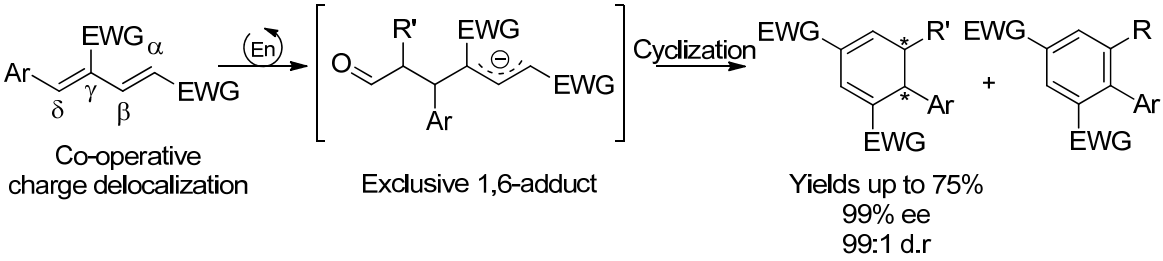

Figure 1. Generation of chiral cyclic dienes and arenes through enamine catalysis (EWG = electron withdrawing group, En = enamine catalysis).

Abstract:

1,3-Butadienes, with appropriately positioned electron-withdrawing substituents, have been shown to be promising substrates in the asymmetric conjugate addition of enamines derived from aldehydes and chiral secondary amine catalysts. To date, these systems have been limited to bis-phenylsulfonyl and bis-ester substituted dienes, due to the difficulty in the synthesis of novel diene substrates [1,2].

Herein, we report the synthesis of novel families of 1,3-butadienes bearing bis-cyano substitution, as well as those bearing a mixture of electron-withdrawing substituents. A Wittig reaction, with modified reaction conditions, is identified as a key step in the synthesis of these challenging substrates.

The utility of these substrates in the asymmetric conjugate addition of aldehydic enamines (Figure 1) has been investigated, resulting in the generation of chiral cyclic dienes in yields of up to 75% with excellent enantioinduction (up to 99% ee and 99:1 d.r, Figure 1, EWG = CN). Low yields of an unanticipated highly functionalized aromatized product were also observed.

References:

1 Murphy, J.J.; Quintard, A.; McArdle, P.; Alexakis, A. and Stephens, J.C., *Angew. Chem. Int. Ed.* **2011**, 50, 5095.

2 Pezzati, B.; Chellat, M.F.; Murphy, J.J.; Besnard, C.; Reginato, G.; Stephens, J.C. and Alexakis, A., *Org. Lett.* **2013**, 15, 2950.

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Design, synthesis and catalytic activity of oxazoline based ligands

Mc Cleary, N.*; Cao, Z. and O'Leary, P.

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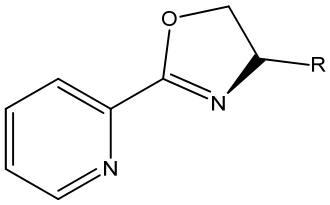
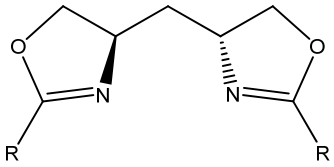


Mono-Oxazoline



Bis-Oxazoline

Abstract:

Today, the majority of therapeutic agents and natural products have chiral centres and therefore can exist in different enantiomeric forms. Many of these function in the body by binding to host enzymes and receptors which themselves contain chiral centres and exist in one enantiomeric form. Due to this, different enantiomers in these binding sites in the body will display different biological activity, some will be less active but some may act in an adverse manner. As a result, methodologies leading to the design and synthesis of enantiomerically pure chiral building blocks are of great synthetic importance.

Compounds containing an oxazoline moiety have become one of the most versatile and commonly utilised class of ligands employed in asymmetric catalysis due to their convenient synthesis and their suitability in a wide variety of metal-catalysed reactions [1]. We have prepared novel oxazoline based ligands, which when coordinated to a metal lead to a chiral catalyst.

Our aim is to create a new family of both mono- and bis(oxazoline) ligands each containing a stereocentre on the carbon adjacent to the coordinating nitrogen atom, incorporating chirality in close proximity to the reactive metal centre. To that end we have successfully synthesised a family of oxazoline based ligands whose coordination chemistry bares a strong resemblance to current examples reported in the literature [2]. We will report on the design, synthesis and catalytic activity of these compounds.

References:

1 Hargaden, G.C. and Guiry, P.J., *Chem. Rev.* **2009**, 109, 2505.
2 Frain, D.; Kirby, F.; McArdle, P. and O'Leary, P., *Synlett.* **2009**, 1261.

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Mechanistic study of the asymmetric oxidation of phosphines under appel conditions: understanding and improving the stereoselection

Carr, D.J.*; Kudavalli, J.S.; Nikitin, K. and Gilheany, D.G.

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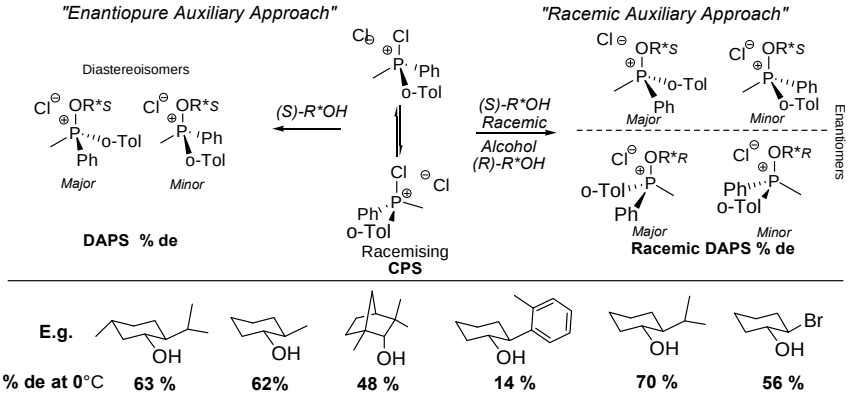

Abstract:

We have previously reported a powerful dynamic resolution of phosphines under asymmetric Appel conditions [1]. By exploring the origin of the stereoselection, the involvement of Berry pseudorotation in the selecting step was first ruled out. This was achieved through the synthesis, and use as test substrate, of cyclic phosphine, 2,3-dihydro-1-phenylbenzo[*b*]phosphole. This allowed us to develop a robust working hypothesis that the stereoselection is *via* dynamic kinetic resolution in the reaction of rapidly racemising chlorophosphonium salts (CPS) with a chiral auxiliary, leading to a pair of diastereomeric alkoxyphosphonium salts (DAPS). The diastereomeric excess (de) of the DAPS derived from a variety of enantiopure chiral alcohols was measured by ^{31}P NMR, showing it to be consistent with the ultimate ee in the phosphine oxide products [2]. In turn this enabled a screen of a variety of ***racemic*** alcohols, allowing use of previously untested cyclohexanols without lengthy enantioselective syntheses. This then allowed us to probe the impact of sterics on stereoselection in a cost and time effective manner leading to a greater understanding of, and significant improvement in, stereoselection.

References:

1 (a) Bergin, E.; O'Connor, C.T.; Robinson, S.B.; Mc Garrigle, E.M.; O'Mahony, C.P. and Gilheany, D.G., *J. Am. Chem. Soc.* **2007**, 129, 9566; (b) Rajendran, K.V. and Gilheany, D.G. *Chem. Commun.* **2012**, 80, 10040.

2 Diastereomeric excess (de) is used to facilitate comparison with the product enantiomeric excess (ee).

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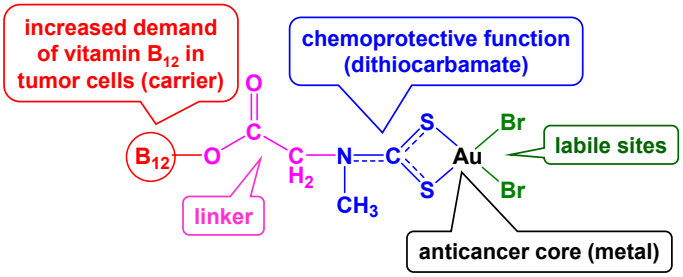
SESSION A2

Rational design of vitamin B_{12}-metal conjugates for the selective delivery of chemotherapeutics into tumor cells

Pigot, R.[1]*; Sonnay, M.[2]; Alberto, R.[2]; Zelder, F.[2] and Ronconi, L.[1]

[1]*School of Chemistry, National University of Ireland Galway, Galway (Ireland).*
[2]*Department of Chemistry, University of Zurich, Zurich (Switzerland).*



Abstract:

Some gold(III)-dithiocarbamato complexes have recently shown promising antitumor activity, both *in vitro* and *in vivo*, together with negligible systemic and organ toxicity [1], although selective tumor targeting is still a major issue.

In order to maximize the impact on cancer cells and minimize side-effects, our latest approaches focus on complexes with tumor targeting properties provided by the coordination of biologically-active ligands, such as vitamin B_{12} (cyanocobalamin). Vitamin B_{12} is an essential nutrient with very low availability. Therefore, rapidly dividing tumor cells, requiring higher amounts of nutrients and energy for cell proliferation, show increased demand of vitamin B_{12} compared to healthy ones [2]. Such avidity of cyanocobalamin can, thus, be exploited for the site-specific delivery of drugs into the tumor by binding vitamin B_{12} (carrier) to an anticancer agent (chemotherapeutics) [3].

We here report on the conjugation of gold(III)-dithiocarbamato derivatives to the 5'-ribose of vitamin B_{12} [4] aimed at combining the anticancer properties and favorable toxicological profile of the gold analogues previously reported with an improved tumor selectivity provided by the conjugated cobalamin acting as delivery carrier, so as to achieve biomolecular recognition and tumor targeting.

Financial support by the National University of Ireland Galway (CoS Scholarship to R.B.) and the COST Action CM1105 (STSM Grant to R.B.) is gratefully acknowledged.

References:

1 Nagy, E.M.; Ronconi, L.; Nardon, C. and Fregona, F. *Mini-Rev. Med. Chem.*, **2012**, 12, 1216.
2 Collins, D.A.; Hogenkamp, H.P.C.; O'Connor, M.K.; Naylor, S.; Benson, L.M.; Hardyman, T.J. and Thorson, L.M. *Mayo Clin. Proc.*, **2000**, 75, 568.
3 Ruiz-Sánchez, P.; König, C.; Ferrari, S. and Alberto, R. *J. Biol. Inorg. Chem.*, **2011**, 16, 33.
4 Zhou, K. and Zelder, F. *Angew. Chem. Int. Ed.*, **2010**, 49, 5178.

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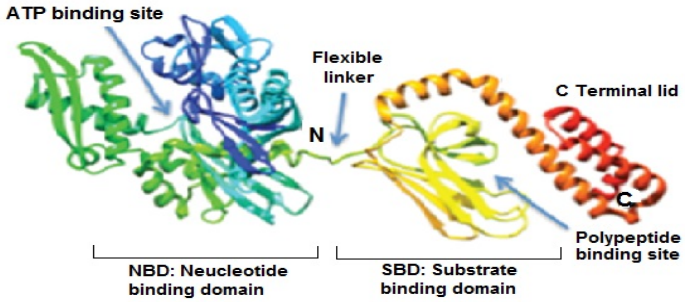
HSP70 as a metallodrug target

McKeon, A.*; Morgan, M.; Platts, J.; Chandanshive, J. and Griffith, D.

Centre for Synthesis & Chemical Biology, Department of Pharmaceutical and Medicinal Chemistry, Royal College of Surgeons in Ireland, Dublin (Ireland).



Abstract:

Cancer is a major cause of death and disease worldwide. Over the past 30 years platinum (Pt) compounds have played a very important and well documented role in treating cancer. The cytotoxicity of Pt drugs is attributed to multiple mechanisms but primarily their ability to form DNA adducts. The clinical efficacy of Pt drugs is limited though by toxicity and chemoresistance (intrinsic or acquired) [1,2]. Since many cancers are intrinsically resistant to Pt-based therapies there is an urgent need to develop novel and innovative therapeutic strategies for combating cancer.

HSP70 is a stress-inducible chaperone, which maintains protein homeostasis during normal cell growth but during a stress response is overexpressed and binds to and stabilises its protein substrates. It is overexpressed in colorectal and prostate cancer amongst other cancers, and is associated with cancer progression, chemotherapy resistance (including against cisplatin) 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 for example. In addition given HSP70 is overexpresed in cancer cells relative to normal cells this effect should be selective. Inhibition of HSP70 is therefore an exciting and legitimate anti-cancer target.

Consequently, we wish to develop novel Pt HSP70 inhibitor drug candidates as potential alternative treatments for colorectal cancer. A summary of cell biology, molecular modelling and synthetic results to date will be described. This research was supported by Science Foundation Ireland under Grant No. [12/IP/1305].

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Ruthenium(II) (BIAN) complexes as DNA metallo-intercalators and exceptionally cytotoxic agents

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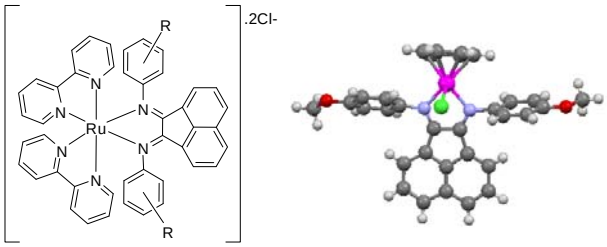

Abstract:

The medical and biological application of ruthenium complexes, both inorganic and organometallic, is a topic of ongoing intense investigation [1,2]. Therefore, a greater understanding of the binding dynamics of photochemically active compounds to biologically relevant targets, including proteins, RNA and DNA is critical. During the past decade, an entire class of complexes has emerged which is dedicated to strong DNA binding, represented by the ubiquitous tris(dipyridyl)ruthenium(II) complex and its related variations [3]. Also, many organoruthenium piano stool complexes incorporating this class of ligands have shown a number of promising anti-tumor activity in recent years [4].

In this work, we introduce a new array of fully characterized Ru(II)-polyazine and organometallic η^6-arene piano stool type complexes incorporating the bis(aryl) acenaphthenequinonediimine (BIAN) ligand. This neutral, bulky α,α-diimine ligand features tunable flanking aryl groups and a naphthalene backbone ideal for base pair intercalation in DNA. Preliminary spectroscopic characterisation of the binding by these complexes to double stranded DNA is presented. Moreover, results of cytotoxicity studies conducted on a newly synthesized and characterized range of piano stool ruthenium(II) complexes which also utilise this ligand system and structure-activity relationships through tuning of the substituents on the BIAN ligand will be detailed.

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Molecular methods at the metallodrug-DNA interface

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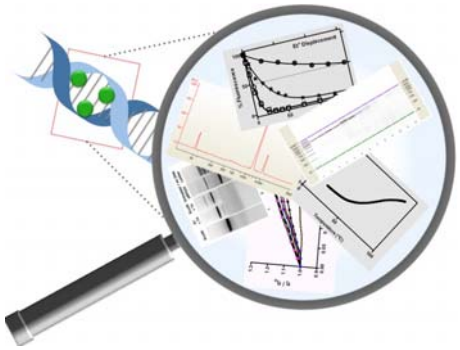

Figure 1. Schematic of analytical techniques used to determine metallodrug-DNA binding.

Abstract:

DNA is an important biomolecule that can be targeted by a variety of metal complexes. Small molecules that bind DNA are important biochemical tools and therapeutics that find application both *in vivo* and *ex vivo* [1]. Here we report a series of *in vitro* techniques and methodologies (Figure 1) to determine the interaction of metallodrugs on DNA. Changes in fluorescence intensities of the intercalator ethidium bromide (EtBr), and minor groove binder Hoechst 33258 when bound to dsDNA in the presence of tested agents, allows us to determine high-throughput binding affinities on families of metal complexes [2,3]. Chemical nuclease activity, site-specific cleavage and endonuclease inhibition can now be identified using "On Chip" microfluidic methodologies that we have devised using the Agilent 2100 Bioanalyzer platform [4].

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SESSION B2

Synthesis of a peptide antibiotic derived from a natural food preservative

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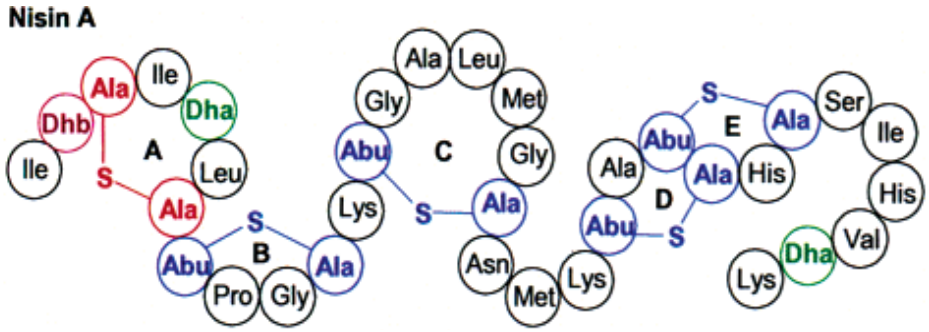

Figure 1. Structure of nisin.

Abstract:

The development of novel antibiotic analogues is vital in the fight against microbial resistance. One area of interest currently being researched is the development of peptides, with known bioactivity, into novel antibiotics [1]. Nisin, a natural polycyclic peptide lanthipeptide of 34 amino acids, containing 5 rings (A-E), is currently used as a food preservative in dairy, meat and tinned food products [2]. It is an antimicrobial agent against Gram positive bacteria, but is unstable at physiological pH; in part due to the reactive dehydroalanine residue at position 5 in the A ring [3]. Development of nisin analogues with enhanced stability, while also maintaining high bioactivity, would greatly enhance the possible use of a nisin analogue as an antibiotic.

One project aim is to synthesise analogues of the A and B rings of nisin (Figure 1) by replacing the Dha 5 with more stable amino acid residues in the A ring using solid phase peptide synthesis (SPPS). The conformational properties of these nisin analogues will be examined by using a range of NMR techniques, as well as molecular modelling. Details of our synthetic efforts to date will be presented.

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Access to biologically important 2-pyrones via C-H activation strategies

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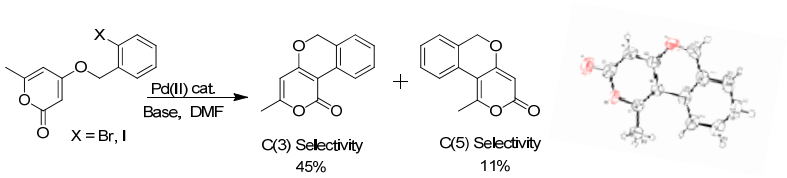

Abstract:

2-Pyrones are important biologically active molecules, highly abundant in bacteria, microbial, plant, insect and animal systems [1]. Related to the 2-pyrone motif in both structure and biological diversity are 2-coumarins, 2-pyridinones and 2-quinolones. Traditional methods of biaryl formation such as Suzuki-Miyaura reactions require prefunctionalisation of both coupling partners. A more atom economic approach is "Direct Arylation" which requires preactivation of only one coupling partner and produces less waste [2,3].

The aim of this project is to synthesise substituted 2-pyrones, 2-coumarins, 2-pyridinones and 2-quinolones *via* intramolecular direct arylation reactions.

Intramolecular cross-coupled products have been successfully obtained on an array of substrates with preferred regioselectivity occurring at C-3. Synthesis of these substrates was carried out using Jeffrey's conditions, *via* a Heck-type reaction. Concerted Metalation Deprotonation (CMD) conditions have also been developed which facilitate this type of transformation.

Intermolecular direct arylation and double C-H activation methodologies were also targeted, extending to the more robust 2-coumarin motif. A good substrate scope is tolerated.

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From heterocycles to cell cycles: isoellipticines as anti-cancer agents

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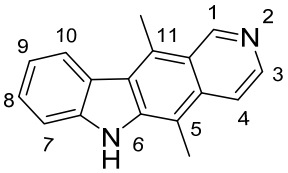

Fig. 1. Ellipticine

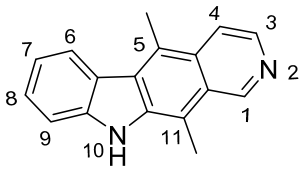

Fig. 2. Isoellipticine

Abstract:

Ellipticine (Fig. 1) is a natural product possessing multimodal cytotoxic activity including DNA intercalation, topoisomerase II inhibition, c-Kit kinase inhibition and restoration of function to mutant p53 protein [1,2]. While ellipticine itself is not a suitable candidate for therapeutic use, derivatives including 2-methyl-9-hydroxyellipticinium acetate and 2-(2-(diethylamino)ethyl)-9-hydroxyellipticinium chloride, have progressed to clinical trials [3,4].

The effect of derivatisation on the isoellipticine template (an isomer of ellipticine, Fig. 2) is uncharted and structural diversification of isoellipticine could lead to drug candidates with a better clinical profile due to enhanced target specificity. Our initial approach to this uses substitutent modification at positions 10, 7 and 2 (salt formation at the N2 position represents a favourable attribute for cytotoxic activity as illustrated by the two most successful ellipticines). A number of novel derivatives of isoellipticine have been synthesised and further derivatised. Preliminary biological testing of novel compounds was performed using a topoisomerase II decatenation assay and via assessment of the anticancer profile using the National Cancer Institute 60 cell line screen for cellular activity [5]. Significant anticancer activity and cell line selectivity will be described, with several of the compounds analysed to date progressing to the Biological Evaluation Committee for *in vivo* studies. Flow cytometry studies have been undertaken to investigate the cellular basis for this intriguing activity.

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Non-viral gene delivery vectors: synthesis and *in vitro* biological evaluation

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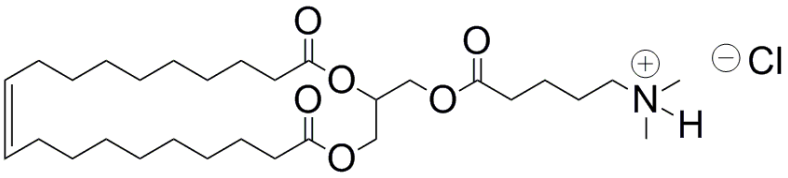

Abstract:

Gene therapy involves the transfer of genetic material into a cell, using a delivery vehicle or vector, to correct either the overexpression, or under-expression of a protein and thus eliminate the genetic abnormality or damage affecting the healthy function of the cell. The current study involves the synthesis and *in vitro* biological evaluation of cationic lipid vectors to achieve the safe and efficient delivery of genetic material into Chinese hamster ovarian (CHO) cells. These vectors are characterised by their ease of preparation and a much lower immune response in comparison to viral vectors.

Our design for a novel, non-viral cationic lipid vector was based on either a macrocyclic or acyclic hydrophobic domain, linked via ester bonds to a glycerol backbone, together with a cationic head group based on either a protonated amine or quaternary ammonium salt. The culmination of our research efforts [1], which includes the design and optimisation of a synthesis route to a library of cationic lipids, together with the results of binding, degradation, cytotoxicity and transfection assays, will be presented. The transfection efficiency and cytotoxicity of our lipids was compared against each other and commercial delivery systems. In fact, we found a number of our cationic lipids outperformed the gold standard lipofectamine 2000.

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SESSION A3

The formation of metal-carbon nanotube composites for applications in non-enzymatic glucose sensing

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Abstract:

The use of composite nanomaterials in electrochemical sensors has been of great interest over recent years due to the useful characteristics they exhibit, with electrocatalytic sensing abilities and large surface areas [1-11] being most significant. These materials can be produced using synthetic [2,3,5,7] and electrochemical [4,6,8-11] means and typically combine metal nanoparticles, including gold [2,4,12], platinum [3,7], palladium [10,11], nickel [8,9] and copper [1,5,6] with a conducing support usually consisting of carbon nanotubes [2,3,5-7,11,12], grapheme [4,8,9] and/or conducting polymers [4,10].

In this present study a gold nanoparticle-functionalised multi-walled carbon nanotube composite (fMWCNT-Au_{nano}) was prepared using a simple synthetic procedure and was used in an electrochemical system for the direct sensing of glucose at neutral pH. This film was encapsulated with a Nafion® membrane to reduce interference from commonly occurring interferants. The use of other metal particles with this film was also examined to investigate any potential improvements.

Transmission and scanning electron microscopy (TEM and SEM), energy dispersive X-Ray analysis (EDX), X-Ray diffraction (XRD), atomic absorption spectroscopy (AAS) and UV-visible spectroscopy (UV-Vis) were employed to characterise the materials. Electrochemical measurements also provided useful information.

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Glucose oxidation at enzyme electrodes under physiological conditions for application to biosensors and biofuel cells

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Abstract:

Immobilisation of a redox enzyme with redox mediators on an electrode surface can provide electrocatalytic response for substrates, such as sugars, important in biosensor and biofuel cell applications. I report, initially, on a simple, novel immobilisation strategy using electrochemically-induced grafting of osmium-based redox mediators onto carbon electrodes, for enzyme electrode fabrication. The redox-active layer is produced upon electrochemical oxidation of alkyl-amine functional groups, distal to a ligand of the redox complex, to form reactive radicals that couple to carbon surfaces, with coupling characterized by XPS and voltammetry.

Thicker films can be produced by addition of nanostructured supports, and by cross-linking alkyl-amine functional groups, distal to a ligand of the redox complex, to the redox enzyme and functionalised polymers, with concomitant adsorption/grafting to the electrode surface. Co-immobilisation of enzyme, redox complex and polymer support using a chemical crosslinker therefore provides a 3-dimensional biofilm for electrocatalysis.

I will thus report on the electrochemical response of enzyme electrodes composed of glucose oxidase, multiwalled carbon nanotubes and a range of redox mediators and polymer supports, in seeking to improve the current density and stability of glucose-oxidising enzyme electrodes under physiological conditions. Overall, a maximum current density of 3.4 mA cm^{-2} at 0.2 V vs. Ag/AgCl, in pH 7.4 phosphate buffer at 37 °C, was achieved for oxidation of glucose, showing promise for application to glucose determination in blood and as an anode in a biofuel cell for electric power generation.

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Non-invasive detection of biological fluids: a new perspective in monitoring pH in saliva and sodium in sweat

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Abstract:

The chemical composition of body fluids contains crucial information about the state of health of an individual. While many efforts have been already directed toward real time analysis of blood and urine, there is still a pressing need for new solutions to non-invasively monitor other fluids like saliva and sweat [1].
Towards this aim, the main technological challenge is the development of devices that are at the same time low-cost, minimally invasive and wearable, so that they could be used for in situ and real-time monitoring of physiological conditions [2]. For example, continuous recording of sodium levels in sweat could be an informative tool to assist clinicians in prescribing a more personalised treatment of diseases such as Cystic Fibrosis [3] and in assessing athletes' performances [4]. Similarly, the monitoring of pH levels in saliva provides valuable information for the treatment of pathologies where physiological mouth conditions are compromised, like in Gastroesophageal Reflux Disease (GERD) [5].
Ion Selective Electrodes (ISEs) are potentiometric sensors designed to detect specific ions in blood and saliva. Using dual-screen printed electrodes as substrates, we were able to reduce their production cost, improve reproducibility, and combine pH^5 and sodium ISEs with solid contact reference electrodes. In our design, the sensors will be interfaced to two miniaturized potentiometric platforms (WIXEL for pH and Tyndall Mote for sodium detection) that were wirelessly connected to a base station. For pH measurements, the device will be accommodated into a gum shield. For sodium detection instead, we will use a microfluidic channel to convey sweat to the electrodes. The mote communication platform was adapted so that it could be worn on the upper shoulder through a fiber strip.

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Identifying sources and chemical composition of atmospheric aerosols using single particle mass spectrometry

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Abstract:

According to the most recent Intergovernmental Panel on Climate Change report [1] (IPCC report on Climate Change, 2007), the largest uncertainty in climate forcing is associated with the composition of atmospheric aerosols. Overall, it is even unsure whether aerosols are warming or cooling the planet. Atmospheric aerosols are also known to have an adverse affect on human health. Fine airborne particles, with diameters less than 2.5 microns ($PM_{2.5}$), have the largest impact on human health due to their ability to reach the lower regions of the respiratory system. The World Health Organization [2] (WHO report on Air Pollution, 2005) reports that exposure to ambient particulate matter reduces life expectancy by one year and accounts for almost 800,000 premature deaths worldwide. Research is therefore required into characterizing the sources and chemical composition of atmospheric aerosols in order to improve our understanding of the effects on human health and climate. On-line analysis of atmospheric aerosol in Cork [3,4], Paris [5], Barcelona, Dunkirk and Corsica was performed using an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) which allowed for the measurement of the size and chemical composition of individual ambient particles in real time in the size range 0.1 to 3 microns. Using source-specific markers, the chemical composition data obtained was used to identify and quantify the various emission sources at the different sites.

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SESSION B3

Tackling neuroblastoma: design and development of PNA based miR-34a mimics

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Abstract:

Neuroblastoma is the most common extra-cranial pediatric solid tumour and the MYCN proto-oncogene overexpression remains its most significant biomarker. MYCN is amplified in ~25% of NB tumours and it is always associated with an aggressive behaviour of the cancer and poor outcome [1], therefore, MYCN is an ideal target for Neuroblastoma tackling. It has been recently shown that miR-34a is able to bind to the 3'UTR of MYCN mRNA inhibiting protein translation and it is the strongest MYCN protein level regulator [2]. By silencing MYCN expression it exerts a massive inhibition on cell proliferation and it is considered a strong tumour suppressor. Peptide Nucleic Acids (PNA) have been identified as suitable analogues to develop miRNA-34a mimics with enhanced properties such as stability and resistance to endonucleases and proteases. Considering the higher affinity and binding stability of PNAs towards cognate mRNAs, the challenge is finding out the shortest oligonucleotide able to silence MYCN expression. PNA constructs of different length have been designed [3] including (a) a seed sequence and/or 3'-supplementary binding site recognising 3'UTR region of MYCN mRNA (b) a peptide carrier able to improve the internalization of the construct (c) a linker (d) a fluorescent tag. The PNA-based miRNAs described herein were prepared by microwave assisted solid phase synthesis and their biological activity will be tested in vitro on Neuroblastoma cell lines. The final aim of the project is elucidation of the minimal requirements for a small molecule to inactivate MYCN transcripts. A computational study of the interaction between the active structures and mRNA along with structural analysis will be translated into the design of novel small molecules to be proposed for a high scale industrial drug manufacture.
Contextually with the ongoing research on PNA analogues with improved physical and chemical properties, a novel chiral PNA monomer analogue was designed and synthesized.

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Stabilisation of paralytic shellfish poisoning toxins in shellfish tissue matrices for the preparation of reference materials

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Abstract:

Reference materials (RMs) are needed for the development, validation and quality control of analytical methods. Various stabilisation techniques have been investigated to observe improvements in the stability of PSP toxins in shellfish tissue matrices and their applicability for the preparation of reference materials both certified and uncertified for use in routine monitoring, quality control and proficiency testing. All materials have been assessed for both short and long-term stability through a reverse isochronous design using two HPLC techniques, with all preparation methods significantly improving toxin stability compared to untreated tissues.

Computational and NMR based mechanistic studies of L-proline derived organocatalysts

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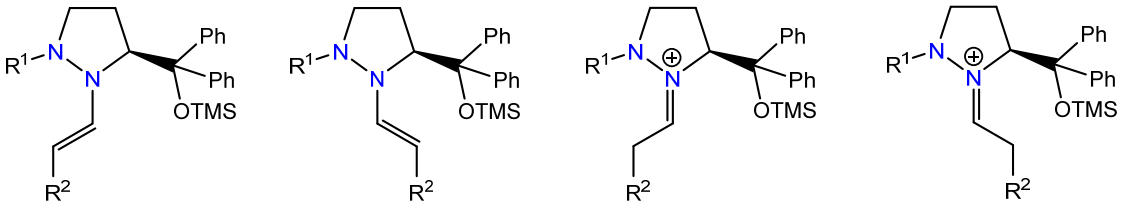

Figure 1. Enamine and iminium ion intermediates of aza-diarylprolinol silyl ethers.

Abstract:

The seminal work of Barbas [1] and MacMillan [2] in the early 2000s saw a huge resurgence of interest in the use of small, strictly organic molecules, as catalysts for asymmetric transformations. While synthetic studies have flourished, mechanistic investigations have not enjoyed as much attention.

In recent years, however, a number of important papers [3-5] have highlighted the use of computational and NMR methodologies for mechanistic studies. To date our work has focused on the use of DFT calculations to elucidate the relative conformational energies of a series of prolinamide and diarylprolinol silyl ether derived intermediates. Structural optimisations using DFT have also been carried out on a series of aza derivatives of the silyl ethers (Fig. 1); these results will be presented.

NMR studies are being undertaken to investigate the formation of intermediates associated with the prolinamide catalysed asymmetric Michael addition of aldehydes to nitroolefins.

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2 Ahrendt, K.; Borths, C. and MacMillan, D., *J. Am. Chem. Soc.* **2000**, 122, 4243.
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IRISH RESEARCH COUNCIL
An Chomhairle um Thaighde in Éirinn

SESSION A4

Activity and coke formation of nickel and nickel carbide in dry reforming: a deactivation model from density functional theory

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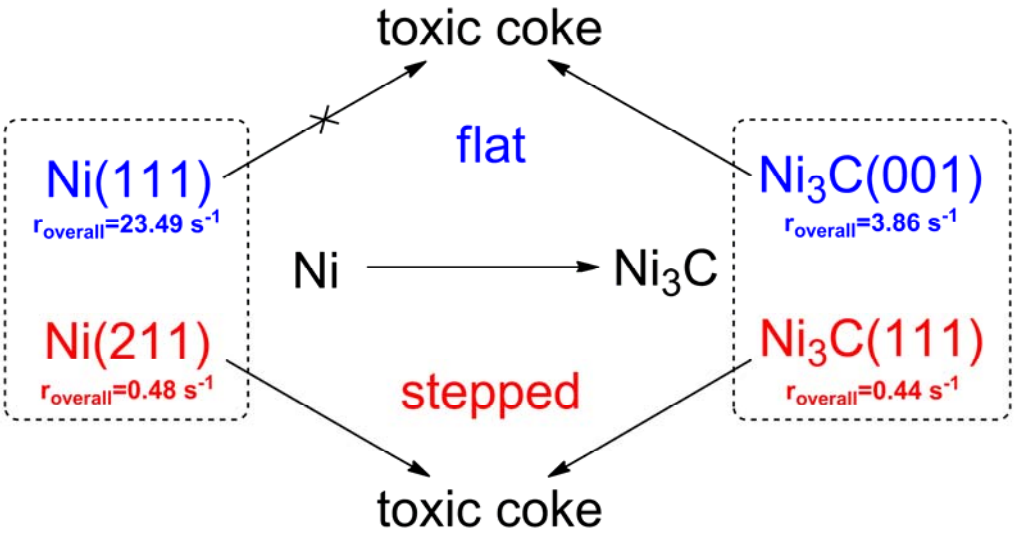

Abstract:

Dry reforming is a promising reaction to utilise the greenhouse gases CO_2 and CH_4. Nickel-based catalysts are the most popular catalysts for the reaction, and the coke formation on the catalysts is the main obstacle to the commercialisation of dry reforming. In this study, the whole reaction network of dry reformation on both flat and stepped nickel catalysts (Ni(111) and Ni(211)) as well as nickel carbide (flat: $Ni_3C(001)$; stepped: $Ni_3C(111)$) is investigated using density functional theory calculations. The overall reaction energy profiles in the free energy landscape are obtained and kinetic analyses are utilised to evaluate the activity of the four surfaces. A deactivation model, using which experimental results can be rationalised, is proposed.

References:

1 Wang, Z., Cao; X.M.; Zhu, J. and Hu, P., *J. Catal.* **2014**, 311, 469.

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AERODynamic surfaces through MUltifunctional COatings (AEROMUCO)

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Abstract:

Aircraft are exposed to environmental phenomena such as ice accretion, insect contamination and particulate erosion which affect the aerodynamic performance of an aeroplane's leading edge. With the increased use of composite materials for lighter aerospace structures, there is a need for protective multifunctional coatings on aircraft surfaces that maintain aerodynamic performance in light of the aforementioned environmental challenges. The AEROMUCO project led by Airbus GI has the purpose of designing, developing, upscaling, applying and validating novel active and passive surface protection systems which address the framework call's goal of the "greening of air transport".

This talk will outline the steps involved in the:

1. Development of multifunctional coatings that reduce in-flight icing and insect adhesion through bio inspired surfaces, ethylene glycol containing polyurethane coatings and in particular hybrid sol gel materials which exploit perfluorinated silane chemistry to impart low surface energy.
2. Generation of enzymatic active surface protection systems through the synthesis of hybrid sol gel coatings incorporating functionalised mesoporous silica which act as nano-reservoirs for enzymes allowing the break down and removal insect residue during flight.
3. Evaluation of the novel surface coatings and treatments
   a. in conjunction with active electromechanical and electrothermal de-icing systems in a large ice wind tunnel testing environment;
   b. by flight tests through high volume insect populations to examine the adhesion performance.

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Design and development of a patterned bio-fuel cell

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Abstract:

The performances of enzymatic fuel cells (EFC) are mainly affected by limitations in stability and power output In order to improve the efficiency of the current bio-fuel cell technology, researchers are striving towards the attempt to obtain a device which can resemble the biological function of enzymes in living matter by mimicking the ability to perform sequential transformation of a substrate to a final product using a sequence of enzymes in which the product of one enzyme serves as the substrate for an adjacent enzyme with the rate of reaction controlled by the concentrations of substrates and co-factors and the activity of the enzymes involved: the enzymatic cascade reaction (ECR) [1]. ECR can alleviate the limitation of a single substrate transformation typical of traditional EFCs by enabling the sequential and more complete oxidation of the fuel. Such sequential reactions mimic cascade reactions in cells. A prototype biofuel cell using this approach was described for the conversion of methanol to carbon dioxide by employing three NAD^+ dependent enzymes: alcohol (ADH), aldehyde (AldDH) and formate (FDH) dehydrogenases. Self-assembled monolayers (SAM) can be used in order to sequentially immobilise a series of enzymes over different electrode areas which are determined by the intrinsic characteristics of the electrodes. The controlled immobilisation of cytochrome c has been used to demonstrate the ability to independently address and pattern the surfaces of two adjacent electrodes with a protein under conditions of neutral pH without affecting the neighbouring surface [2]. The same approach is used to specifically pattern and immobilise enzymes involved in a cascade reaction. The immobilisation of ADH and AldDH at two adjacent gold electrodes has been shown using 3,3'-dithiodipropionic acid di(N-succinimidyl ester) as electrode modifier for covalent attachment of the enzymes.

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Towards a hydrogen economy: the investigation into the oxygen evolution reaction (OER) using transition metals

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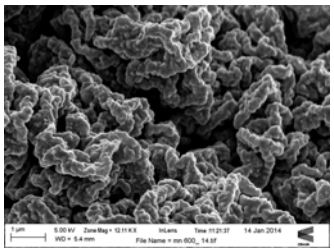

Figure 1. SEM image of manganese only electrocatalysts.

Abstract:

Alkaline water electrolysis has been proposed as an environmentally inoffensive route to the production of the large volumes of hydrogen gas required by a possible hydrogen economy [1]. In practice, the efficiency of water electrolysis is limited by the large anodic over-potential of the oxygen evolution reaction (OER) [1]. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials, with the aim of achieving useful rates of active oxygen evolution at the lowest possible over-potential, in order to optimize the overall electrolysis process.

In the present work, we focus on the redox properties and electrocatalytic behaviour with respect to anodic oxygen evolution of manganese and ruthenium oxide electrodes prepared at different molar ratios in aqueous alkaline solution. These films can be prepared simply via thermal decomposition of a metal salt [2]. The structure and morphology of the thermally decomposed oxide materials are examined using thin film XRD, high resolution SEM and FTIR. The redox behavior of the resulting oxide films is investigated as a function of molar ratio and annealing temperature using cyclic voltammetry. The kinetics of the OER at these films have been studied using a range of electrochemical techniques including steady-state polarization. In particular, Tafel slopes and reaction orders with respect to hydroxide ion activity are determined. Interestingly, the electrochemical performance for the films is strongly dependent on the molar ratio used, as evident from Figure 1. The electrocatalysts will be compared and contrasted under a number of Key Performance Indicators (KPI's) including Turnover Frequency, stability, cost and initial oxygen evolution overpotential.

References:

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SESSION B4

Metal Organic Frameworks based on carboxylate functionalised tetrazole ligands

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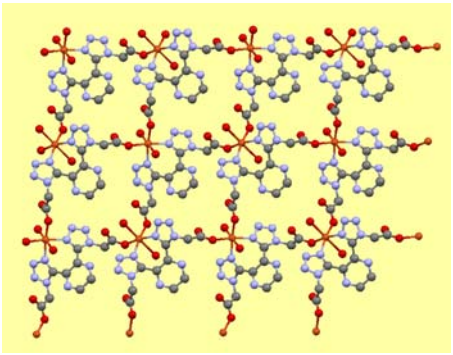

Abstract:

Metal Organic Frameworks (MOFs) are a class of porous materials that have seen rapid and extensive growth in recent years [1]. This growth is not only due to their interesting topological structures but also for their potential applications in the fields of luminescence, gas adsorption, catalysis and drug delivery [2].

Amongst the ligands used in the construction of these frameworks, multidentate N- or O-donor building blocks have received extensive attention [3]. Our research involves reactions of *in situ* generated carboxylate functionalised 5-substituted tetrazoles with metal(II) salts, which gives access to a number of coordination polymers with diverse connectivity and interesting structural features. X-ray crystallography reveals the presence of free metal coordination sites. The direct formation of frameworks bearing chelating ligand sites that are open to metal insertion is rare, since typically metal binding at these sites would occur during framework synthesis. This provides potential possibilities of host-guest interactions and post-synthetic modifications. We envisage that these frameworks will provide a platform for the insertion of a wide variety of metal centres, leading to a broad range of properties and applications.

References:

1 Furukawa, H.; Cordova, K.E.; O'Keeffe, M. and Yaghi, O.M., *Science* **2013**, 341, 974.
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3 Zhang, X.M.; Zheng, Y.Z.; Li, C.R.; Zhang, W.X. and Chen, X.M., *Cryst. Growth Des.* **2007**, 7, 980.

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New materials for solar cell applications

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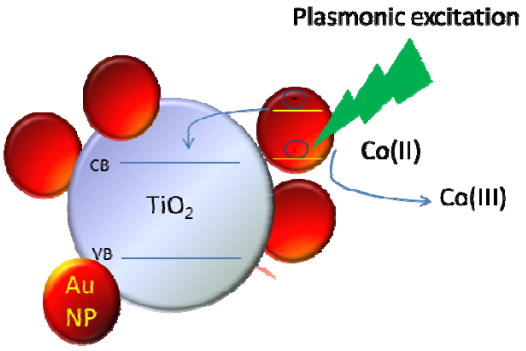

Figure 1. Proposed mechanism for the generation of plasmonic photocurrent.

Abstract:

We present the preparation and photophysical studies of a novel gold nanoparticle - titanium dioxide composite system. The material was prepared by the electrophoretic deposition of gold nanoparticles into a porous nanoparticulate titanium dioxide film, creating a photoactive electrode. The composite film demonstrates a significant increase in the short circuit current (I_{sc}) compared to unmodified TiO_2 when excited at, or close to the plasmon resonance of the gold nanoparticles. We employ a thermal ripening process as a method of increasing the I_{sc} of these electrodes and also as a method of tuning the plasmon peak position, with a high degree of selectivity. Photo-electrochemical investigations reveal that the increase in photocurrent is attributed to the generation and separation of plasmonically generated electrons at the gold/TiO_2 interface and also the inter-band generation of holes in AuNPs by photons with $\lambda < 520$ nm. Theoretical modeling results are in perfect agreement with the experimental observations of the processes leading to enhanced photo-current.

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Tapping into the triplet state - New applications and possibilities with 1,10-phenanthroline based Ir(III) and Ru(II) complexes

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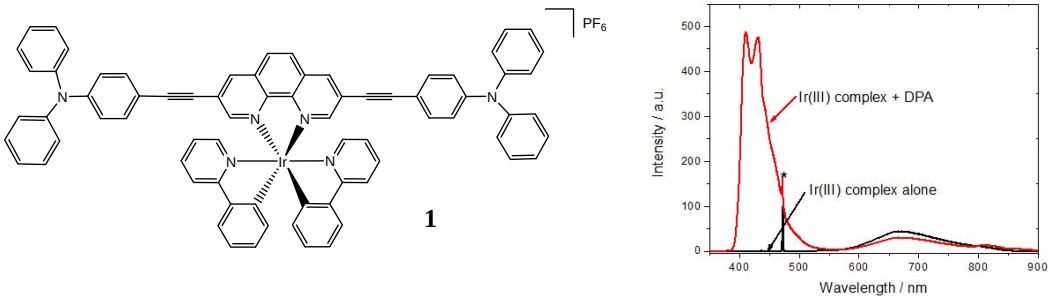

Figure 1. The chemical structure of **1** and its upconverted fluorescence in the presence of DPA (9,10-diphenylanthrance) as annihilator (λ_{ex} = 473 nm).

Abstract:

Tapping into the long-lived triplet excited states and enhanced inter-system crossing of heavy transition metal centres is important for next-generation photocatalysts and opto-electronic devices. In order to convert low-energy photons into useful higher energy ones, similar metal complexes are being investigated to engage in triplet-triplet annihilation (TTA) [1-3]. TTA upconversion makes use of the interactions between a light-harvesting triplet photosensitiser (the donor) and a suitable emitting organic acceptor. An efficient donor is key to this process, and this work focuses on the synthesis and photophysical investigation of a series of 1,10-phenanthroline-derived Ir(III) and Ru(II) donors. To ensure strong UV-Vis absorption and promote the formation of long-lived triplet states, the π-conjugation of the 1,10-phenanthroline ligand was extended to include arylacetylide light-harvesting antennas at the 3,8-positions. The novel Ir(III) complex (**1**, figure 1) shows strong absorption of visible light (ε = 55,000 $M^{-1}cm^{-1}$ at λ = 480 nm) and an exceptional upconversion quantum yield (up to 23.2%). The spectra demonstrate that excitation of the donor (at λ = 473 nm) leads to strong, higher energy fluorescence from the organic acceptor (λ ~ 400 nm).

References:

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3 Nattestad, A.; Cheng, Y.Y.; MacQueen, R.W.; Schulze, T.F.; Thompson, F.W.; Mozer, A.J. and Schmidt, T.W., *J. Phys. Chem. Lett.* **2013**, 4, 2073.

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Extraction of high value products from seaweed for biomedical applications

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Abstract:

Brown seaweeds are evolutionarily and chemically different from terrestrial plants. They contain many potential high value feedstocks, e.g. carbohydrate polymers (alginates, fucans), aliphatics (sterols, halocarbons), aromatics (polyphenols) and pigments. In recent years, the bioactive of marine compounds are being increasingly recognised in antioxidant, anticancer, anti-inflammatory, anti-tuberculosis, anti-obesity, and anti-angiogenic therapies. For example, fucosterol was previously shown to be the dominant sterol present in *Ascophyllum nodosum* [1], and one of its breakdown products, saringosterol, has shown some tentative evidence for anti-tuberculosis activity [2]. Phlorotannins (polyphenols) have shown some radical scavenging activity [3], which is of interest in reperfusion injuries (e.g. ischemic heart disease). To unlock their full commercial potential, better separation methods are needed to isolate compounds that translate to industrial scale up. This project specifically investigates the potential extraction of high value compounds from *Ascophyllum nodosum* and their potential application in bone therapeutic. The aims of this work include: (1) to optimise suitable "green" methods for the extraction and purification of high value products, e.g. Fucoidan from *Ascophyllum nodosum,* (2) to screen their bioactivity and (3) test the extracts which show activity on cell cultures so their effects can be monitored. Results to date have shown methanol has been used to effectively extract fucoxanthin from *Ascophyllum nodosum*. Other results have indicated that oleic and linoleic acid, respectively, are the two most abundant fatty acids found in *Ascophyllum nodosum.*

References:

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PLENARY

The molecules of murder

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Abstract:

The crime of murder by deliberate poisoning has always held a terrible fascination, not least because of the secrecy surrounding its planning and the difficulty inherent in its detection. Crime has a very great appeal as evidenced by the sales of detective books and the popularity of TV crime series. The presentation will examine a selection of such crimes from the point of view of the forensic scientist and the toxic agents involved. Crimes involving both natural and synthetic poisons will be covered. The presentation will highlight the role of the analytical chemist in solving murder by poisoning. Their task is often more difficult than finding the proverbial needle in a haystack and they play a key role in all kinds of substance abuse. It will also become clear that the chemicals that nature produces can be at least as deadly as any produced by humans.

POSTERS

Poster	Presenter	Title
1	L. Barry, UL	*Semiconductor-metal hybrid nanostructures*
2	F. Bertoli, UCD	*Unveiling the dark side of the protein corona: a study on its cellular uptake and evolution*
3	H. Prydderch, DCU	*The effect of aromatic groups on the antimicrobial toxicity of ionic liquids derived from phenylalanine and mandelic acid*
4	H. Daly, RCSI	*Off to on switching cellular uptake responsive NIR fluorescent nanoparticles*
5	B.M. Davis, NUIM	*2D-fluorescence spectroscopy of the Group II metal atoms, strontium and barium, isolated in the solid rare gases (RG = Ar, Kr and Xe)*
6	A. Delaney, ITT	*Design and fabrication of printed electrochemical immunosensors for progesterone testing – AURO-QUANT*
7	R. Fagan, DIT	*Development of visible light active photocatalytic materials for environmental applications*
8	E. Forde, RCSI	*Developing a series of novel Host Defence Peptide prodrugs for use in cystic fibrosis*
9	I.J. Godwin, TCD	*Water oxidation catalysis at RuO_2/NiO mixed oxide electrodes*
10	M.P. Grace, NUIM	*The stability of high concentration whey protein systems and the influence of pH and salt*
11	C. Healy,TCD	*Synthesis and functionalisation of novel transition-metal substituted polyoxometalates*
12	R. Herron, UCD	*The efficient hydrolysis of ammonia borane using SBA-15 supported Co and Ni nanoparticulate catalysts*
13	B. Irwin, TCD	*Novel photochromic molecular switches generated from dithienylethene*
14	S. James, NUIM	*Effect of mutagenesis on the phase transitions of human gamma-D crystalline*
15	R. Kavanagh, ITT	*Glycolsylated coumarins – New therapeutic target*
16	L. MacLean, ITT	*Antioxidants: a unifying chemical motif?*
17	D. Malone, ITT	*The stereoselective synthesis of biologically important peptide building blocks using organocatalysis*
18	C.S. McCallum, QUB	*A "green" catalytic hydrogenolysis process for the depolymerisation of suberin from cork bark*
19	E. McGillicuddy, UCC	*Comparison of Aerosol Time of Flight Mass Spectrometer (ATOFMS) measurements with off-line techniques for determining metal concentration in atmospheric particles*

20	T.J.P. Mc Givern, RCSI	*Development of a new class of Pt(II) inhibitor conjugates*
21	W. Messina, UCC	*Impedance sensors for biomedical & bioassay applications*
22	Z. Molphy, DCU	*Copper phenanthrene oxidative chemical nucleases*
23	D.P. O'Brien, UL	*Investigation of the kinetics of phosphorus pentoxide in ethanol*
24	T. O'Hara, ITT	*The development of an electrochemical cytotoxicity sensor "TOXOR" – Applications in environmental toxin monitoring*
25	J. O'Sullivan, NUIM	*Synthesis of functional calixarenes for the selective detection of metal ions*
26	S.P. Shannon, UCD	*Nano-assembly of spin crossover complexes*
27	M. Sheehan, UL	*Growth of crystalline transition metal silicide and germanide nanowires within a high boiling point solvent system*
28	E. Sheehy, UCD	*Asymmetric synthesis of the bis-acetylene natural product falcarinol*
29	R. Smith, UCD	*Synthesis and investigation of α-thioglycosides and their reactivity*
30	F. Torri, RCSI	*Synthesis of unnatural C-nucleosides for artificial DNAs*
31	Z. Ude, RCSI	*Novel multi-functional metallodrug candidates as potential cancer therapeutics*
32	N. Willis-Fox, TCD	*Tuning the emission colour of conjugated polymer-di-ureasil hybrid materials: composition, energy transfer and white light emission*
33	H.J. Winfield, UCC	*Arresting cell growth by novel indolocarbazoles functionalised by Lossen Rearrangement*
34	C. Magee, NUIG	*Chain transfer to solvent in the radical polymerization of tert-butylacrylamide*
35	Y. Li, NUIG	*An experimental study of isobutene ignition delay time at elevated pressures*
36	A.W. McDonagh, NUIG	*Synthesis of α-glycolipids based on triazoles via α-glycosyl azides*
37	L. Kerins, NUIG	*Anomerization and anomeric effect in uronic acids*
38	N. Crushell, NUIG	*Towards a metal-based catalyst capable of the cleavage of the RNA component of human telomerase*
39	E.P. McCarney, TCD	*Lanthanide driven synthesis of novel luminescent self-assembly molecules and materials*

Semiconductor-metal hybrid nanostructures

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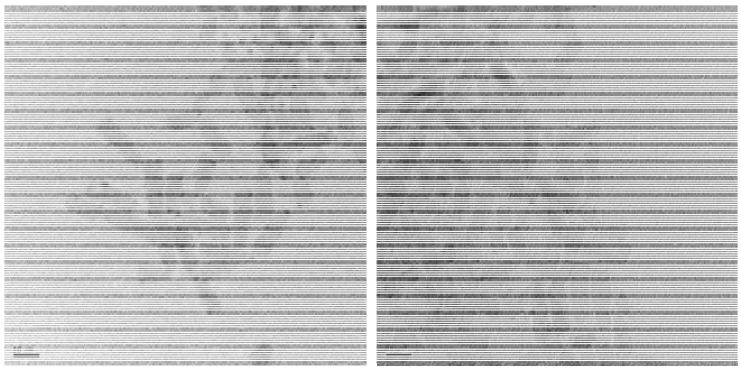

Figure 1. TEM images of CZTS nanorods with multiple gold tips.

Abstract:

There has been an increased interest in the formation of semiconductor-metal hybrid nanostructures. The introduction of metal tips to form these semicoductor-metal hybrid nanostructures is thought to be an important integration step for nanocrystal devices. An example of this is Au-CdSe where enhanced photocatalytic reactions are possible in solution through charge separation at the metal-semiconductor interface [1]. Electron transfer via redox processes in a protein immobilised on metal tipped nanorods was detected at a substrate which has potential for sensor applications [2]. The metals tips on the semiconductor nanocrystals could also act as anchor points for electrical contacts. Recent advances have led to the formation of metal tips, in particular gold or silver, onto cadmium based nanocrystals/nanorods (CdS/CdSe/CdTe). The gold tips formed through an organic phase reduction method or a phase transfer method. Silver tips were formed using a phase transfer method. Control over the metal tip sizes and over the formation of assymetrical/symmetrical tips on the ends of the nanorods instead of multiple tips all over the nanorods was achieved [1,3]. Here we investigate the formation of a semiconductor-metal hybrid with other nanocrystals e.g. CZTS using the organic phase reduction method and the phase transfer method as previously used for control of tip formation on CdS/CdSe/CdTe.

References:

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Unveiling the dark side of the protein corona: a study on its cellular uptake and evolution

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Abstract:

Nanomaterials (and specifically nanoparticles), as a result of their unique properties (like small size and their large surface area), offer great promise for drug delivery systems and medicine therapies [1,2]; therefore, in last ten years, a great scientific effort has been employed in determining how nanoparticles interact with biological systems and, specifically, with cells. Different studies have showed how nanoparticle - cell interactions are governed by different parameters, one of the main being the layer of proteins and other biomolecules adsorbed on the nanoparticle surface from the surrounding biological media (protein corona) [1]. Although the composition and extracellular stability of the protein corona of various nanoparticles have been characterized and studied [3] little is still understood about the intracellular uptake and evolution of this layer and how nanoparticle characteristics (like surface properties) affect these processes. Here we fluorescently labelled the protein corona formed on polystyrene nanoparticles with different surface properties (amino and carboxyl modified) and we follow its intracellular uptake and evolution with different fluorescence based techniques and we emphasize the fundamental role the surface plays in the corona final destiny; specifically we show how different surfaces leads to different kinetics in the processing of the corona proteins by the cells. To achieve a better understanding of the final fate of the proteins of the corona subcellular fractionation techniques have been employed to isolate the organelles in which the corona localized and different techniques (like fluorescent microscopy, flow cytometry, 1 D SDS PAGE and mass spectrometry) have been used to understand the processing of these proteins from the cells. The findings show that, when corona proteins reach the lysosomes, they are there degraded by the lysosomal proteases. We then compare the amount of proteins the two nanoparticle types bring into the lysosomes with the amount of serum internalized in normal conditions, and we have found that nanoparticles may bring on their surface an unsuspected amount of proteins and traffic them to specific organelles.

References:

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3 Monopoli, M.P.; Aberg, C.; Salvati, A. and Dawson, K.A., *Nat. Nanotechnol.* **2012**, 7, 779.

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The effect of aromatic groups on the antimicrobial toxicity of ionic liquids derived from phenylalanine and mandelic acid

Prydderch, H.*; Jordan, A.; Ventura, S.P.M.; Gurbisz, M.; Ghavre, M.; Ferreira, F.M.M.; Gonçalves, F.; Beadham, I.; Quilty, B.; Coutinho, J.A.P.; Coleman, D.; Špulák, M.; Garcia, M.T. and Gathergood, N.

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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. ILs must not persist in the environment and should be non-toxic or of limited toxicity to the environment. The Gathergood group has proposed that using renewable resources to form ILs could improve the eco-toxicity of the compounds. Thus, work has been carried out on the synthesis of ILs with a bio-derived anion, namely the amino acid phenyalanine and mandelic acid [1,2].

ILs from phenylalanine with various headgroups and aromatic substituents were synthesised. Modification of the headgroups on the phenylalanine scaffold has allowed for toxicity studies to be carried out on the effect of aromatic and non-aromatic headgroups. A study focusing on the imidazolium headgroup showed that imidazolium ILs containing phenylalanine were non-toxic (IC_{95} > 2 mM) to the twelve fungi strains and eight bacteria strains screened against.[1] Dipeptide amino acid examples were also examined in this study and were also found to have low toxicity.

A series of eight ILs from mandelic acid with imidazolium and pyridinium headgroups were synthesised to allow for the investigation of toxicity on modifying the heterocycle, aromatic ring substitution, ester group, and proximity of cation to aromatic ring.[2] 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.

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Off to on switching cellular uptake responsive NIR fluorescent nanoparticles

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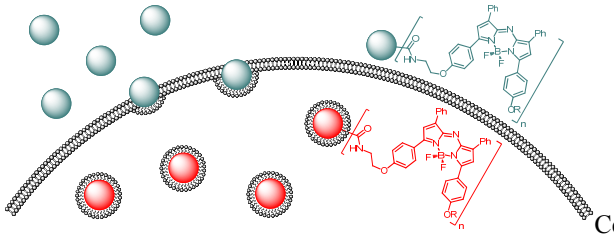

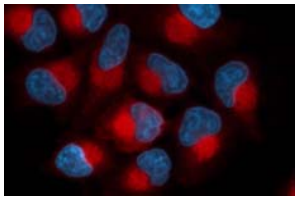

Abstract:

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].

The design, synthesis, characterization and *in vitro* illustration of cellular uptake activated *off* to *on* switchable fluorescent 60 nm nanoparticles will be outlined.

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2D-fluorescence spectroscopy of the Group II metal atoms, strontium and barium, isolated in the solid rare gases (RG = Ar, Kr and Xe)

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Abstract:

In recent years, our Group at Maynooth has successfully employed luminescence spectroscopy to probe the site occupancy of guest metal atoms isolated in rare gas (RG = Ar, Kr and Xe) solids at cryogenic temperatures. Metal atoms such as Mg, Zn, Cd [1], Mn [2], Na [3] and Eu [4] have been studied, all of which exhibit spherically symmetric, S ground states and strong $P \leftarrow S$ type transitions in absorption. Excitation spectra recorded of the $P \leftarrow S$ transition possess a characteristic three-fold splitting pattern. This structure has been attributed to Jahn-Teller coupling in the degenerate P excited state and as a result, the isolation of these metal atoms has been inferred to occur preferentially in sites of high (cubo-octahedral) symmetry. The present contribution focuses on the larger metal atoms, strontium (Sr) and barium (Ba), and is an important extension to the current body of work since both metal atoms exhibit an $ns^2\ ^1S_0$ ground state and their $P \leftarrow S$ transitions serve as a sensitive probe of the surrounding RG environment. Concentration experiments have yielded the deposition conditions required to achieve optimal atomic isolation in Ar, Kr and Xe matrices. Annealing experiments have identified the thermally stable sites of isolation of the guest atom. 2D-fluorescence (excitation/emission) has proved to be vital in both M/RG systems to deconvolute complicated absorption profiles into multiple, distinct excitation features. Nanosecond time-resolved spectroscopy of the site-selected emission bands has also assisted in this regard. Comparing the M-RG (M=Sr, Ba) diatomic bond-lengths [5,6] with the radii of the available cubic sites within each RG host, reveals a substantial size mismatch. This strongly suggests that larger, multi-atom vacancies within the host lattice must be considered. Indeed, the excitation spectra recorded in each M/RG system display a variety of patterns, ranging from the classic Jahn-Teller threefold split bands to pi-like doublets and broad, unstructured bands. Thus, experimental evidence strongly suggests that the trapping of Sr and Ba atoms in the RG solids occurs in both spherically symmetric crystalline sites on the one hand and in defect sites on the other.

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Design and fabrication of printed electrochemical immunosensors for progesterone testing – AURO-QUANT

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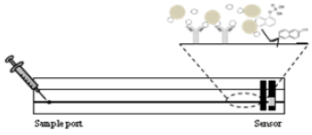

Figure 1. Schematic representation of Immuno-Cap - illustrating the structure of a single-channel device and the competitive immunoassay protocol for progesterone.

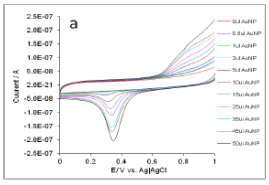

Figure 2. Cyclic voltammogram profiles for increasing Au nanoparticle concentration following anodic deposition and subsequent cathodic stripping – confirming signal generation for surface confined Au.

Abstract:

Profitability in the dairy industry is heavily dependent on the accuracy of progesterone 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 progesterone in bovine milk and serum, yet practical implementation of a sensitive, rapid, low cost test remains a technical challenge. The end goal of this study envisages development of a thin-layer mesofluidic system integrating rapid flow immunochromatography to electrochemical detection for the on-site monitoring of progesterone in cow's milk. The Immuno-Cap device may be described as a micro-capillary biosensor and is based on redox activity of nanogold as the signalling element of the competitive ELISA format. Figure 1 shows a schematic of the antibody coated micro-channel, and a redox responsive electrode-sensor (Au stripping wave Figure 2). Synthetic research approaches will investigate compounds capable of both co-ordinating to gold nanoparticles through thione functionality while also providing a link to the target molecule, progesterone. The assay principle is based on a competitive format between free progesterone in the sample and progesterone labelled with gold nanoparticles (immunoconjugate) for binding sites on the internal wall of the capillary, which has been coated with anti-progesterone antibody. The quantity of conjugate arriving at the electrode is detected electrochemically and is related to free progesterone concentration in the sample.

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Development of visible light active photocatalytic materials for environmental applications

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Abstract:

The modification of titanium dioxide (TiO_2) by elemental doping is an emerging area for increasing the efficiency of visible light photocatalysis [1-3]. Significant research attention on doping titanium dioxide with non-metals is one method which has been applied to the preparation of TiO_2 with the intention of altering the ability to be visible light active (Figure 1). Co-doping TiO_2 with two or more dopants to achieve a combined dopant effect or improved effect when compared to single source doping was investigated. The co-dopants used were ammonium fluoride (NH_4F) and ammonium hexafluorophosphate (NH_4PF_6).

These dopants were incorporated as into the titanium dioxide at the time of synthesis and were subsequently heat treated using a novel microwave treatment to allow these additives to diffuse into the titania lattice. The samples prepared at various concentrations of dopant were then characterised using XRD, Raman, FT-IR, diffuse absorbance, XPS and BET analysis. Photocatalytic activity of these samples was tested using various light sources. These tests were conducted using rhodamine 6G dye and in some cases with (a cyanotoxin) Microcystin-LR (MC-LR) as model pollutants. Further studies are underway to optimise the preparation of visible light active photocatalysts for their degradation of various organic compounds.

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Developing a series of novel Host Defence Peptide prodrugs for use in cystic fibrosis

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Abstract:

Introduction: Host Defence Peptides (HDPs) are short antimicrobial peptides forming part of the innate immune system. Deficiencies in these peptides can lead to enhanced susceptibility to infections, e.g. in cystic fibrosis (CF). HDPs can be toxic at therapeutic concentrations and their endogenous expression is strictly controlled. Significant research has focused on their use as a new class of anti-infectives despite their shortfalls. This study focuses on a series of novel HDP prodrugs, with their charge masked by a promoeity designed to be removed by the enzyme Neutrophil Elastase (NE), high concentrations of which are associated with CF. Previously, HDP prodrugs have been developed with NE-dependent activity and improved cytotoxicity [1]. Here we describe how further improvements in selectivity were achieved with further modification.

Methods: Enzyme-labile peptides were synthesised and incubated with enzyme standards to confirm lability. Both oligoglutamic acid and PEG were investigated as new pro-moieties and new active HDPs were used. The MICs and bactericidal activities of the parent sequences and the pro- sequences against *P. aeruginosa* were compared, with or without NE-rich CF bronchoalveolar lavage (BAL) fluid. The effect of both the parent and pro- sequences on human cells was also investigated.

Results and Discussion: While modification of the pro-moiety did not produce any improvement in selectivity, the new HDP sequences lead to greatly improved selectivity. In the presence of BAL fluid, the activity of the pro-sequences was greatly increased, indicating BAL-dependent activation. Cytotoxicity was greatly reduced compared to previous peptides and cytokine release studies indicated no immunogenicity. Pro-HDPs such as these are promising candidates in the search for new therapeutics in conditions such as CF.

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Water oxidation catalysis at RuO_2/NiO mixed oxide electrodes

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Abstract:

Electrochemical water splitting via alkaline water electrolysis is currently an extremely active research area of intense topical international interest. This is due to the need for the development of a clean, reliable and sustainable method for large scale production of high purity hydrogen gas for use as a fuel in a potential hydrogen economy [1]. However, one of the grand challenges fully utilising alkaline water electrolysis for hydrogen production is in the large anodic overpotential associated with the oxygen evolution reaction (OER). Over the past 30 years considerable research effort and resources have been focused on the development and improvement of novel anode materials, with the aim of achieving useful rates of the OER at the lowest possible overpotential and cost in order to improve the economic viability of this technology. Dimensionally stable anode (DSA®) electrodes, based on RuO_2 and IrO_2 currently exhibit the lowest overpotential for the OER at practical current densities [2]. Despite their excellent OER performance, the relative high cost of these materials, in particular iridium, combined with their poor long term chemical stability in alkaline media renders their long term use as anode materials for water electrolysers impractical. Because of this problem we have attempted to overcome this problem by using oxides/hydroxides/ oxyhydroxides of first row transition metals which offer comparable OER performance but at significantly lower cost [3,4]. In this work we have studied RuO_2/NiO mixed oxide electrodes prepared by thermal decomposition for use as potential water oxidation catalysts. Addition of just 10 mol% RuO_2 to a NiO electrode was found to decrease the oxygen evolution reaction (OER) onset potential by 20% with increasing additions having significantly diminishing returns. The OER current densities for the 25/75 mol% RuO_2/NiO electrode was found to significantly increase when preconditioned by application of prolonged polarisation regimes with the Tafel slope also decreasing from *ca*. 75 mV dec^{-1} to *ca.* 50 mV dec^{-1}. NiO prepared by thermal decomposition was found to behave in a similar manner to other nickel oxides [5,6] prepared using different methodologies.

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The stability of high concentration whey protein systems and the influence of pH and salt

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Abstract:

The stability of milk proteins over a range of solution conditions is an acute issue for processing in the dairy industry. In particular, high concentration protein solutions are desirable, but inherently unstable due to protein aggregation. The mechanisms leading to aggregation are complex, but include stresses imposed by heating and changes to pH and salt concentrations. Therefore, there is a need to understand the processes leading to aggregation for this protein system [1].

α-lactalbumin is a calcium binding whey protein and accounts for 28% of the protein present in milk. When α-lactalbumin is heat denatured, it unfolds, often leading to aggregation. This process is influenced by solution conditions. We have previously shown that the relative stability of protein solutions against thermal denaturation can be assessed by quantifying the reversibility of the process by DSC [2]. Here we show how the temperature at which unfolding occurs (T_m) changes with solution conditions and assess whether the unfolding process is reversible and if this is related to T_m and solution conditions. The effect of calcium salts in particular influenced the thermal stability of α-lactalbumin. Two protein forms are present at calcium concentrations; apo α-lactalbumin (no calcium) and holo α-lactalbumin (with calcium) [3]. As the calcium concentration increases, the holo form is dominant and is further affected by changes in calcium concentration.

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Synthesis and functionalisation of novel transition-metal substituted polyoxometalates

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Abstract:

Polyoxometalates (POMs) are a diverse class of entirely inorganic, anionic metal-oxo clusters with wide-ranging applications, principally in nanotechnology and catalysis [1,2]. Incorporating first-row transition metals into these structures can yield a vast array of interesting mixed-metal systems with unusual structures. These can be manipulated with relative ease due to their ligand-stabilised nature [3]. We have developed such a series of large molybdenum-manganese clusters of the general formula $[(C_4H_9)_4N]_2[Mo_{10}Mn_6O_{30}L_4(H_2O)_6(R_1\text{-}PO_3)(R_2\text{-}COO)_2]$. The ligand L and the moieties R_1 and R_2 may all be easily manipulated, either via ligand substitution or via in-situ ligand formation, thus yielding a significant array of structures [4]. These compounds display strong oxidative capability which may be of significance.

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The efficient hydrolysis of ammonia borane using SBA-15 supported Co and Ni nanoparticulate catalysts

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Abstract:

One of the main factors delaying the development of PEM fuel cell powered vehicles is the safe and efficient storage and transport of sufficient quantities of H_2 fuel. $H_{2(g)}$ has a very low volumetric energy density (0.01 kJ L^{-1}) and high pressures and low temperature storage systems are incompatible with transportation usage due to associated costs and safety issues. For this reason, there is considerable research effort in storing H_2 at ambient temperatures and pressures.

Ammonia borane (AB) has a high gravimetric density of hydrogen that can be released at low temperatures *via* a hydrolysis reaction using suitable catalysts [1].

$$NH_3BH_{3\ (aq)} + 2H_2O_{\ (l)} \rightarrow (NH_4)BO_{2\ (aq)} + 3H_{2\ (g)}$$

Noble metal catalysts [2] are particularly efficient for promoting this reaction, but are unsuitable for practical applications due to their high cost and limited availability. While first row transition metals have also been employed in this reaction, their efficiencies have not been comparable to those of noble metals [1].

This work focuses on the use of cobalt and nickel nanoparticles deposited on SBA-15 as catalysts for the hydrolysis of AB in aqueous solutions. The preparation, characterisation and application of a range of these materials is described.

These catalysts can efficiently hydrolyse AB, with a bimetallic CoNi catalyst showing increased reaction rates when compared to analogous monometallic Ni and Co containing catalysts, suggesting a possible synergistic effect.

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Novel photochromic molecular switches generated from dithienylethene

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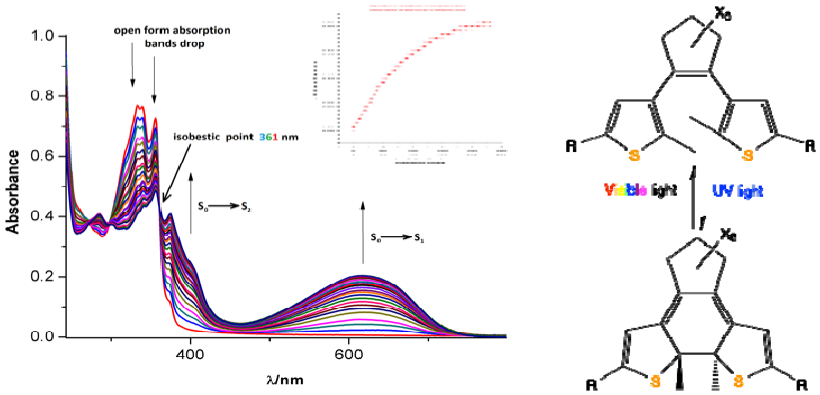

Figure 1. (left) Absorbance spectrum of (**2**), from open to closed, recorded after 30 s intervals under short range UV radiation and (right) reversible photocyclisation reaction of a DTE based switch upon UV-Vis light irradiation, open (top) to closed (bottom).

Abstract:

Information storage is at the forefront of materials science due to the exponential increase in demand for faster, more efficient, higher density data storage units and for miniaturised devices. Light-driven photochromic switches form one of the most active area of research due to their use in devices which operate at both molecular and supramolecular scales [1-3]. Herein a series of dithienylethene based switches have been designed and synthesised with appended polyaromatic ligands of increasing conjugation. The work demonstrates the effect of increased aromaticity of both the appendages and of the thienly core to the molecules' photo physical properties. Studies of these systems (Fig. 1) allow insight into the use of these switches in memory devices and the effect the aromatic moieties have on the switches colour change, photochemical quantum yield and emission profile, as well as photostationary state conversion. Further fine tuning of the synthetic design, redox and photophysical properties are on-going to establish the potential of the new systems in a range of device applications.

Funding agency acknowledgement: Science Foundation Ireland (SFI).

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Effect of mutagenesis on the phase transitions of human gamma-D crystallin

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Abstract:

Human gamma-D crystallin (HGD) is one of the major structural proteins of the eye lens, soluble to concentrations exceeding 400 mg/ml. Single mutations in HGD are associated with several childhood cataracts. Phase diagrams for several of these protein mutants have been measured and reveal that the phase boundaries are shifted compared with the native protein, leading to condensation of protein in a physiologically relevant regime [1-3]. Using HGD as a model, we have constructed a phase diagram for several double mutations of HGD, incorporating two single amino acid substitutions for which phase diagrams are already known. Upon mutagenesis, very little change in protein structure occurs. Interestingly, characteristic features associated with the single amino acid substitutions are maintained in the double mutant protein. While these proteins are not of interest physiologically, they offer insights into interparticle interactions associated with "patchy" or anisotropic colloidal particles.

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Glycolsylated coumarins – New therapeutic target

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Abstract:

Coumarin and derivatives of coumarin are known to be one of the most biologically active classes of molecules. They have a wide variety of applications such as in the treatment of cancer [1], antibacterial infections [2], as anticoagulant [3] and as antifungal therapies [4]. We have been interested in copper-based coumarin complexes for a number of years [5-8] and have identified a series of compounds which have shown good anticancer activity against a number of cancerous cell lines. However, most of these complexes have been found to be insoluble in water and their cytotoxicity necessitated the use of DMSO in the testing protocol. For a molecule to have a good therapeutic profile, it is desirable that the water solubility is increased. Therefore our current work focuses on the development of coumarin-based ligands which have increased aqueous solubility. To increase water solubility of the complexes, the addition of a sugar moiety to the coumarin ligand was a desirable approach. The sugar component of the molecule would increase the solubility of the complex and should be recognised by receptors on the cell surface of cancer cells. The work mainly focuses on the preparation of novel glycosylated coumarin ligands.

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Antioxidants: a unifying chemical motif?

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Abstract:

Copper(II) complexes with mixed oxygen-nitrogen donor ligands have previously shown anti-candida [1,2], antibacterial activity [3] and cytoxicity [4,5] on selected cancer cell lines. Furthermore studies have shown them to exhibit superoxide, SOD, and catalase, CAT, mimetic activity [5,6]. The human body through normal 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 species through their dismutation to less harmful compounds. When oxidative stress is out of balance, these ROS cause induced cell damage which can lead to disease. Inflammatory conditions such as Alzheimer's, arthritis and tumours are characterised by high levels of ROS, therefore copper(II) complexes could provide a new therapeutic approach in their treatment through their ability to mimic these enzymes. In this research, a series of copper(II) complexes containing coumarin derived Schiff base ligands, and a series of complexes containing a combination of ligands including salicylate derivatives, 1,10-phenanthroline, phthalates, acetate, benzimidazole and 2,2-bipyridine will be synthesised. SOD and CAT mimetic activity will be evaluated using *Saccharomyces Cerevsiae* cells under oxidative stress, and the protective effect of the copper(II) complexes determined.

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The stereoselective synthesis of biologically important peptide building blocks using organocatalysis

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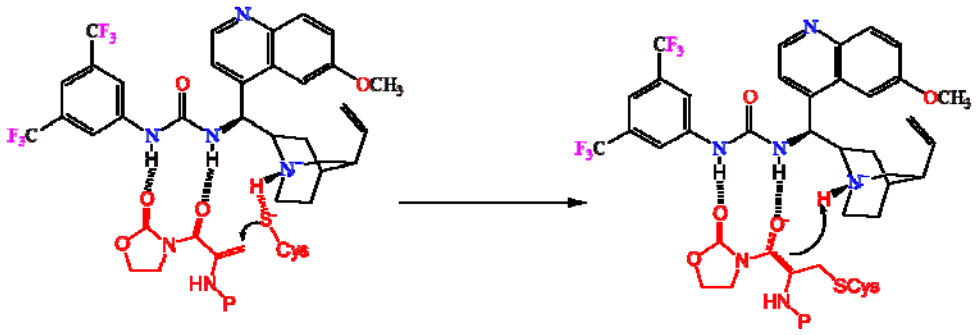

Abstract:

In the US, approximately 60% of staphylococcal infections in hospitals are now caused by methicillin-resistant *Staphylococcus aureus* (MRSA) [1]. Therefore, it is important that new antibiotics are developed, while those already in use, such as the antibacterial peptide nisin, are modified to become more stable and effective. A key feature in the 34 peptide chain of nisin, is the dipeptide lanthionine, which is involved in the formation of the ring structures that are vital for its biological mechanism of action [2].

Currently, the main lanthionine syntheses in the literature involve the reaction of cysteines with protected bromoalanines or iodoalanines which can readily dehydrohalogenate to give dehydroalainine (Dha), which leads to unwanted diastereomeric products [3]. This project, to date, has focused on the non-stereoselective synthesis of lanthionines. The aim now is the synthesis and use of chiral organocatalysts, such as bifunctional thioureas derived from cinchona alkaloids, to promote the stereoselective synthesis of lanthionines, using more easily synthesised and stable starting materials. These starting materials will subsequently be optimised to facilitate improved binding to the catalysts, ultimately improving the overall diastereomeric outcome of the reaction.

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A "green" catalytic hydrogenolysis process for the depolymerisation of suberin from cork bark

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Abstract:

Research into the structure of tree barks and their potential for generating high added value chemical products has accelerated in recent years with an increased understanding of the main biopolymer components: lignin, cellulose, hemicellulose and suberin. Cork contains a high percentage of the natural polyester suberin which gives long chain hydrocarbons as well as aromatic products when depolymerised under controlled conditions. Following on from the new methods of biomass depolymerisation developed at Queen's University [1] this work is focussed on developing the downstream process to a commercially viable operation and reducing the environmental impact of the overall process by the introduction of "greener" solvents and the maximum reuse of any by-products from the system.

The new separation methods include working with ion exchange resins which have been shown previously to facilitate the removal of fatty acids from complex mixtures [2] and pH controlled separation exploiting the different pKa values for the phenolic and fatty acid components present in the product stream. A new "green" solvent system has been an area which has also been developed moving away from dioxane towards the sustainably-sourced solvent methyl-THF. Further advancements presented here are the new method for quantitative analysis of the products in the mixture using a combination of NMR spectroscopy with HPLC and use of a new support matrix in regards to the catalyst.

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Comparison of Aerosol Time of Flight Mass Spectrometer (ATOFMS) measurements with off-line techniques for determining metal concentration in atmospheric particles

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Abstract:

The concentration of metals in atmospheric aerosols is traditionally measured using off-line techniques, with particles being collected onto a substrate which is later analysed using techniques such as ICP-MS, XRF and IC. These methods quantitatively determine the metal component of particulate matter, but suffer from poor time resolution. This leads to short-lived events being missed. Techniques such as PIXE allow samples to be analysed with an hourly resolution. However, none of these off-line techniques can provide information on the mixing state of metals within the particles, which is invaluable in the identification of their sources. The interest in measuring the mixing state of individual aerosol particles has led to the development of single particle mass spectrometers. One such single particle instrument is the ATOFMS, which provides size resolved single particle dual ion mass spectra in the size range 100 nm to 3000 nm. This allows the characterisation of the primary composition of single particles along with the determination of secondary species present in the particle.

The ability of the ATOFMS to determine the presence of metals in ambient particles was utilised during a sampling campaign in Barcelona (Spain) to determine if the ATOFMS can be used to measure metal concentrations in real-time. The ATOFMS ion signals for the metals of interest were compared with measurements made using PIXE. The strongest correlations were found for comparisons between the ATOFMS and PIXE measurements for several metals including Al, Fe, Zn, Mn and Pb. The improved correlations for these metals is likely due to them having a specific source, with several of the metals such as Pb, Zn and Mn also occurring in short sharp peaks in concentration these factors may result in the ATOFMS ion signal responding to changes in concentration in a more proportional fashion. Several comparisons between the ATOFMS ion signal and the PIXE mass provided poor correlations, with the ATOFMS ion signal intensity not being proportional to the ambient concentration for Ca, Cr, Cu, K, Na and Ni. The reason for the poor correlations with the quantitative techniques may be due to the matrix effects associated with the mixing state of the particle being sampled. The mixing state can affect the ionisation of the metal in sampling with the ATOFMS.

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Development of a new class of Pt(II) inhibitor conjugates

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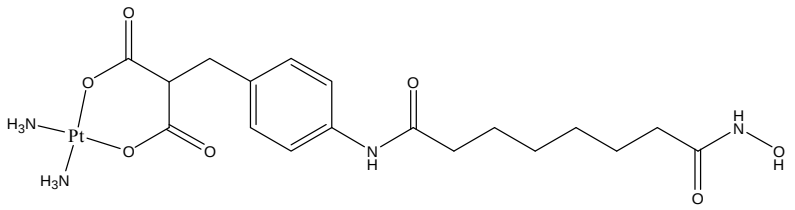

Figure 1. Chemical structure of *cis*-[Pt(NH_3)$_2$(malSAHA-2H)] possessing dual DNA binding and HDAC inhibitory activity.

Abstract:

Cancer, as a disease is a persistent problem worldwide despite public elucidation and treatment regimes. Of all cancer therapies, Platinum (Pt) based drugs continue to play a significant role in modern clinical oncology. Despite their clinical approval the use of Pt based drugs is hindered due to a number of issues including: cytotoxicity, lack of selectivity towards a range of cancer cell types, high dosage regimes and an increasing resistance of cancerous cells towards Pt based drugs. As such, there is an urgent need to develop novel drugs which overcome these drawbacks.

There has been an active interest in the search for new molecular targets beyond DNA with a view to therapeutic exploitation. Histone Deacetylase (HDAC) enzymes are involved in the control of chromatin structure. These enzymes have been investigated for this purpose, the inhibition of which results in the suppression of tumour cell proliferation. Suberoylanilide hydroxamic acid (SAHA) first gained approval by the FDA in 2006 was the first HDAC inhibitor (HDACi) of its kind to enter the clinic.

Previous work in The Marmion group has developed and synthesized a novel Pt(II) drug candidate which possesses dual DNA binding of Pt(II) and HDAC inhibitory activity of SAHA, cis-[Pt(NH_3)$_2$(malSAHA-2H)] [1] (Figure 1). Consequently, we investigated other molecular targets with a view to generating new Pt(II) inhibitor conjugates. Recent advances and synthetic methodology shall be discussed.

References:

1 Griffith, D.; Morgan, M.P. and Marmion, C.J., *Chem. Comm*. **2009**, 44, 6735.

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Impedance sensors for biomedical & bioassay applications

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Abstract:

Major biological challenges such as development of novel minimally invasive medical devices, smart sensing components integrated within surgical tools, real time point of care diagnostics, development of novel anti-cancer drugs and cancer detection are targeted research goals in the health, medicine and biotechnology sectors. This poster describes three research projects that integrate impedance sensors on devices. The first project aims to develop a 'SMART' needle which will improve the safety of Ultrasound-guided peripheral nerve block (USgPNB) by providing the clinician impedance data to identify tissue type at the needle tip. The second project involves the development of a probe integrated with an impedance sensor for early screening and detection of breast cancer. The final project describes the use of Electric Cell-substrate Impedance Sensing to perform real time cell health monitoring. The research described fits extremely well within several of the research National Reprioritisation areas including the priority areas of medical devices and diagnostics, and the platform science and technology areas of basic biomedical sciences and nanotechnology. These projects are excellent examples of how BIO and ICT converge to enable the progression of innovative research by adapting existing technology (impedance sensing) and translating it for the development of a needle/probe/sensor technology that can be applied in the fields of cell based biosensors, USgPNB and for cancer screening.

USgPNB refers to a set of medical procedures which facilitate surgical operations or are performed to treat acute or chronic pain. The needle tip position relative to the target nerve is crucial to the safe but effective practice of USgPNB. Nerve injury may occur if the needle used for nerve block enters the substance of the nerve. Our solution will facilitate more sensitive identification of a target nerve(s); real-time guidance of a needle toward the nerve(s), enabling precise deposition of an anesthetic agent around the nerve(s). In the current climate where the health sector and Irish public demand better and more reliable tools for breast cancer detection, the delivery of such a device would enable clinicians to identify earlier the presence of a malignant tumour. The multi-disciplinary nature of this project brings together researchers and clinicians to tackle the societal challenge of detecting breast cancer at an early stage in order to further reduce mortality rates by advancing the minimal invasive technology that can complement the existing gold standards. Cell based biosensors are analytical measurement devices which use mammalian cells as the sensing element. The response of the cells provides an understanding of the effects of the analyte at a physiological level. Impedance measurements are centred on the fact that whole live cells, at low signal frequencies, are excellent electrical insulators. Cell growth and migration leading to increased coverage of an electrode surface result in increased electrode impedance. A change in impedance value is directly related to attachment and spreading of cells on the surface of the electrodes. These changes in impedance values can be used to explain cell behaviour and to test for new drug substances. This poster will therefore present several examples for the development and application of impedance sensors, highlighting cross-disciplinary research with the goal of delivering impact from excellence.

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Copper phenanthrene oxidative chemical nucleases

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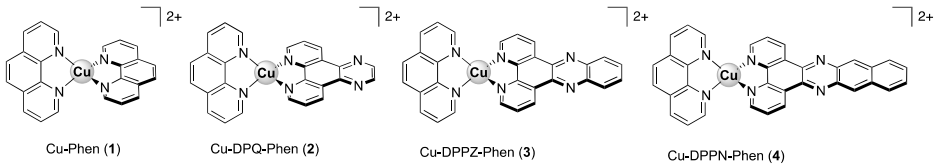

Abstract:

Since the discovery of the first synthetic chemical nuclease, $[Cu(phen)_2]^{2+}$ **(1)** has served as an important template for the construction of small molecule DNA damaging reagents. However, there are numerous limitations associated with its use including a reliance on exogenous oxidant and reductant required to generate DNA-reactive copper "oxo" species [1]. Designer metal-chelating phenazine ligands have shown outstanding potential within Ru^{2+} DNA-selective binding probes, however the question remains unanswered regarding their biological activity within Cu^{2+}complexes [2,3]. Here we report the synthesis of a series of bis-chelate Cu^{2+} phenanthroline-phenazine cationic complexes $[Cu(DPQ)(Phen)]^{2+}$ **(2)**, $[Cu(DPPZ)(Phen)]^{2+}$ **(3)** and $[Cu(DPPN)(Phen)]^{2+}$ **(4)** (where DPQ = dipyrido-quinoxaline, DPPZ = dipyrido-phenazine and DPPN = benzo[*i*]dipyrido-phenazine). The ultimate aim of the study was to investigate how the systematic extension of the ligated phenazine ligand influences DNA recognition and oxidative degradation, through a number of biological assays including thermal melting, chemical nuclease activity, DNA binding/quenching and interactions with superhelical pUC19. We also described a novel "on chip" method designed for the Agilent 2100 Bioanalyser to quantify dsDNA degradation with high precision. The incorporation of designer phenazine ligands in the $[Cu(phen)_2]^{2+}$ model pronounces DNA recognition and intercalation with significant enhancement to the dynamic binding constant for $[Cu(DPQ)(Phen)]^{2+}$ and $[Cu(DPPZ)(Phen)]^{2+}$. To our knowledge these binding constants are the highest reported to date for any existing copper(II) phenanthrene complex and greatly surpass the $[Cu(phen)_2]^{2+}$ cation by ~60 fold [4].

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Investigation of the kinetics of phosphorus pentoxide in ethanol

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Abstract:

Hydroxyapatite (HA) is a commercially significant bioceramic. An effective route to production is combustion synthesis using phosphate and calcium precursors dissolved in ethanol [1]. The phosphate precursor is prepared by dissolving phosphorus pentoxide in ethanol. Understanding the chemistry of this solution is important to developing an overall understanding of the process.

Solutions of phosphorus pentoxide in ethanol at varying concentrations are produced under anhydrous conditions; all samples use ethanol in excess. Additional samples are prepared with the addition of water as a reactant. All samples are analysed titrimetrically [2] to determine phosphate content.

Phosphorus pentoxide reacts completely with ethanol. Given time, the solution stabilises to contain equal molar quantities of mono- and di-ethyl phosphate. The excess of ethanol does not affect this behaviour. Higher temperature accelerates the overall reaction.

Addition of water results in more mono-ethyl phosphate being produced, with the additional production of small quantities of phosphoric acid.

References:

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The development of an electrochemical cytotoxicity sensor "TOXOR" – Applications in environmental toxin monitoring

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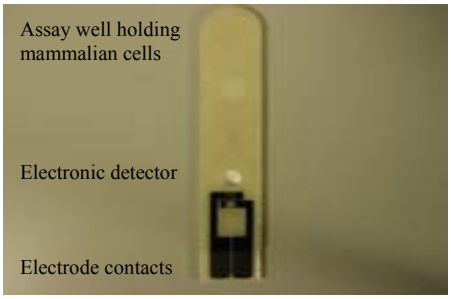

Figure 1. Prototype "TOXOR" device with fluidic release system, assay well and electrochemical detector.

Abstract:

Chemicals from industrial and agricultural sources can have a negative effect on human health and the environment. The REACH directive EC (1907/2006) was introduced by the European Union in June 2007 and is concerned with registration, evaluation, authorisation and restriction of chemical substances that may pose a risk to human health and the environment. This places the responsibility on industry to manage any risks from chemicals and provide safety information for them. Mammalian cell biosensors are valuable tools that can be used to assess the cytotoxicity of chemicals. The "Toxor" electrochemical cytotoxicity sensor presented here (see Fig. 1) is a mammalian cell electrochemical biosensor that measures changes in cellular enzyme activity following exposure of cells to toxic chemicals. It is envisaged that this device could be exploited in the screening of industrial and environmental toxins and has the potential for pharma/drug testing applications. The integrated electrochemical/fluidic sensor has the ability to measure the activity of the enzyme acid phosphatase in A549 human lung epithelial cells. Acid phosphatase catalyses the conversion of 2-naphthyl phosphate to 2-naphthol and is indicative of metabolically active cells. Immobilised cells exposed to toxic chemicals such as pentachlorophenol, nickel chloride showed a decrease in acid phosphatase activity which was detected electrochemically, allowing IC_{50} (50% reduction in acid phosphatase activity) values of toxic chemicals to be reliably determined.

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Synthesis of functional calixarenes for the selective detection of metal ions

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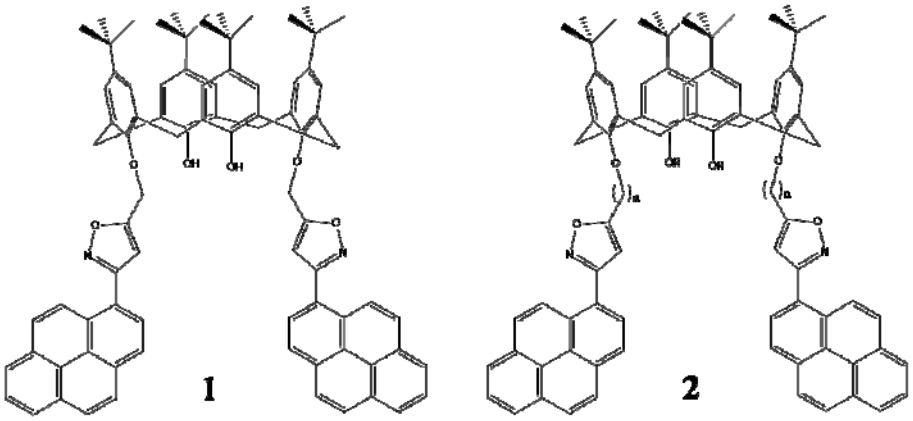

Pyrene Isoxazole Calixarene (PIC) **R ≠ H, n ≠ 1**

Abstract:

Functional calixarenes are attractive sensors of both cationic [1] and anionic [2] species. Recent work in our laboratory has established the potential of the pyrene-isoxazole functionalised calixarene, (PIC), **1**, to selectively detect Cu^{2+} ions in the presence of a range of other metal cations [3,4]. The mode of interaction between the ion and the host molecule is important and to further study this relationship new calixarene derivatives without free hydroxyl groups and with extended spacers between the calixarene core and the pyrene-isoxazole moieties have been designed. This poster reports the synthesis and structural characterisation of these new calixarenes, **2**.

References:

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2 Sutariya, P.G.; Pandya, A.; Lodha, A. and Menon, S.K., *Analyst* **2013,** 138, 2531.
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4 Maher, N.J., *PhD Thesis NUIM* **2013** and unpublished results.

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Nano-assembly of spin crossover complexes

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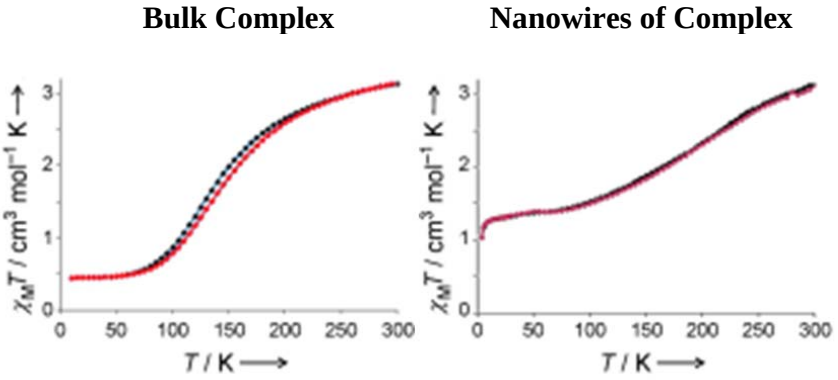

Figure 1. Plots of $\chi_M T$ vs. T for the bulk powder and the templated Fe(III) SCO nanowire sample.

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 identify if there is any change to their physical properties on this scale. Spin crossover (SCO) complexes possess 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. A unique property that can occur in SCO systems is cooperativity [2]. This effect can lead to a hysteresis loop which is vital for the integration of SCO complexes into devices.

The dimensional reduction of SCO complexes has been observed to have an effect on the magnetic behaviour of the materials. 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 as seen in Figure 1 [3]. Here, we now probe SCO properties of 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.

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Growth of crystalline transition metal silicide and germanide nanowires within a high boiling point solvent system

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Abstract:

Transition metal silicides and germanides are a broad set of materials which are finding a number of potential applications in a variety of areas, including microelectronics, optoelectronics, photovoltaics and thermoelectrics. The inherent compatibility of transition metal silicides with silicon make these materials particularly exciting for microelectronic applications. In particular, transition metal silicide NWs are gaining intense interest as a potential replacement for current copper interconnects, where the low resistivities combined with the stable crystal structure of the NWs may offer an attractive alternative to the pure metal.

Here, we report a simple glassware based approach to grow copper silicide NWs in high yield on a copper substrate within the vapour phase of a high boiling point organic solvent (HBS) [1]. The use of the vapour portion of the HBS as a reaction medium is essential to reach the temperatures required for precursor decomposition and NW growth. NW growth is initiated through the thermal decomposition of a suitable organometallic silicon precursor. Prior to NW formation, a non-uniform thin film of copper silicide crystallites is formed on the surface. Once the surface is covered, the crystal habit changes from micrometre sized crystallites to anisotropic NWs with an average diameter of 108 nm. The lengths of the NWs are tunable according to the reaction time.

This approach can also be used to grow nickel germanide NWs from bulk nickel foil using a suitable organometallic germanium precursor. These NWs can be grown up to 8 μm in length and exhibit tapering along the length, with an average diameter of ~100 nm at the root of the NW and an average diameter of ~40 nm at the tip.

References:

1 Geaney, H.; Dickinson, C.; O' Dwyer, C.; Mullane, E.; Singh, A. and Ryan, K.M., *Chem. Mater.* **2012**, 24, 4319.

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Asymmetric synthesis of the bis-acetylene natural product falcarinol

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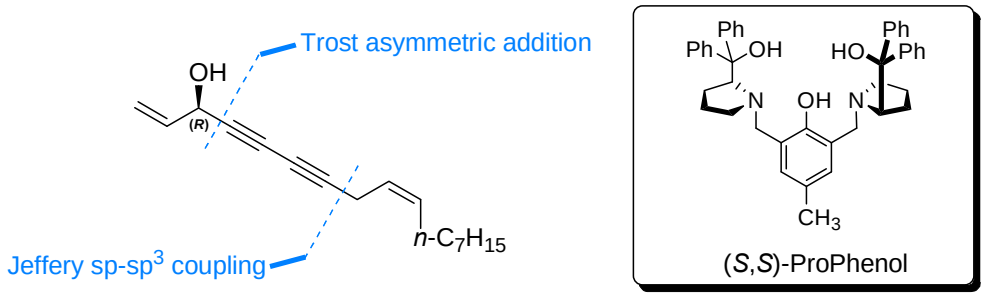
[2]*Teagasc Food Research Centre, Dublin (Ireland).*



Abstract:

Falcarinol is a highly unsaturated 17-carbon compound, with a single stereogenic centre in the 3-position, and a *Z*-alkene in the 9-position. Found in plants, in particular the families *Apiaceae* (e.g. carrot and parsnip) and *Araliaceae* (e.g. ginseng and ivy), the elucidation of the stereochemistry at the 3-position has caused some confusion, partly because both enantiomers have been isolated from different sources [1,2]. These compounds are known to have a range of biological activities, and studies have revealed falcarinol to have anti-inflammatory, anti-bacterial, anti-fungal effects and show cytotoxicity against some cancer cell lines [3,4].

We have carried out a short, convenient synthesis of (±)-falcarinol, which on resolution gave access to both enantiomers of the compound, augmenting the natural supply and facilitating isolation [5,6]. Additionally, an asymmetric adaptation of our synthesis of (+)- and (−)-falcarinol has also been executed using a dinuclear zinc ProPhenol system developed by Trost and co-workers [7]. These studies, along with ongoing efforts to resolve regioselectivity issues encountered, will be presented.

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Synthesis and investigation of α-thioglycosides and their reactivity

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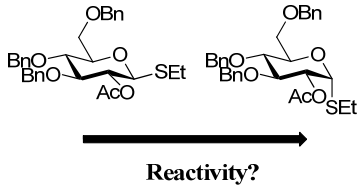

Abstract:

Thioglycosides are among the most widely used and versatile classes of glycosyl donor in modern carbohydrate synthesis. For many years, research in this area has been heavily limited to compounds with a β-anomeric configuration. This is primarily due to the typically low yields and poor selectivity associated with attempted syntheses of α-*S*-glycosides using conventional approaches. However, recent work by the Zhu research group has led to an efficient and stereoselective method for the synthesis of α-glycosyl thiols [1]. Our research has focused on exploring the potential applications of these thiols, particularly their ability to serve as straightforward precursors to their corresponding thioglycoside donors.

Various factors governing the reactivity of thioglycosides have been extensively studied, particularly reactivity modulation by protecting groups. This armed/disarmed concept introduced by Fraser-Reid [2] has been further expanded in recent years by Demchenko's study of the O-2/O-5 co-operative effect, resulting in the classification of superarmed and superdisarmed donors [3]. We wish to add a new dimension to the means by which thioglycoside reactivity can be tuned by investigating the influence of anomeric configuration upon the activation of these compounds. It is well known that β-glycosides exhibit higher nucleophilicity due to increased lone-pair repulsion with the endocyclic oxygen, implying they may undergo faster reaction with glycosylation promoters [4]. However, the anomeric effect results in a noticeably longer α-anomeric bond. Our current aim is to determine which of these effects predominates by using controlled glycosylation conditions, working towards a system for orthogonal activation of thioglycosides based on anomeric configuration.

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Synthesis of unnatural *C*-nucleosides for artificial DNAs

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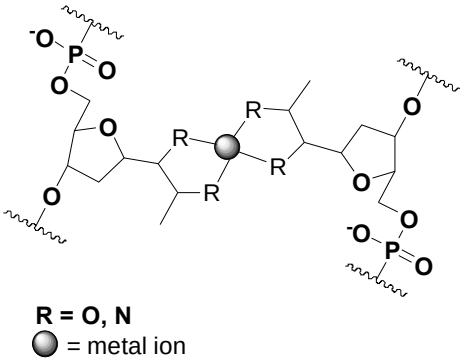

Figure 1. Metal complex with *C*-nucleotides

Abstract:

Many examples of unnatural *C*- and *N*- oligonucleotides for the preparation of artificial DNA, replacing the hydrogen-bonded natural base pairing, trough metal complexation, have been reported to date [1,2]. Based on these findings, a project to design novel analogues with the nucleobase portion substituted by a bidentate chelating functional group that act as DNA base pair forming double helixes is under development, as shown in Figure 1 [3]. Here the synthesis of a nucleoside from a cheap and readily available starting material (i.e. deoxyribose), with a metal coordinating hydroxamic acid moiety will be described.

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Novel multi-functional metallodrug candidates as potential cancer therapeutics

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Abstract:

The first platinum-based anti-cancer chemotherapeutic, cisplatin, was granted clinical approval in 1979. To date, only 3 platinum drugs have gained full global approval as platinum-based anti-cancer therapies. Their widespread application and efficacy is however hindered by their toxic side effects, limited activity against many human cancers and susceptibility to acquired drug resistance.

As a consequence, many investigations into new molecular targets which may present unique opportunities for therapeutic exploitation have been carried out. In recent years, histone deacetylase (HDAC) enzymes have been identified as novel cancer targets, the inhibition of which suppresses tumour cell proliferation. The Marmion research group has designed and synthesised novel anti-cancer bifunctional platinum drug candidates which possess both DNA binding and HDAC inhibitory activity [1-4]. Building on this research, we have been developing other HDACi with a view to binding to metals and generating a library of novel metal-HDACi complexes which may overcome the drawbacks associated with classical platinum drugs. A summary of results to date will be described.

This material is based upon works supported by the Science Foundation Ireland under Grants No. [07/RFP/CHEF570] and [11/RFP.1/CHS/3094]. We also gratefully acknowledge the Programme for Research in Third Level Institutions (PRTLI), administered by the HEA for funding. We thank also colleagues in COST CM1105 for fruitful discussions and collaborations.

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Tuning the emission colour of conjugated polymer-di-ureasil hybrid materials: composition, energy transfer and white light emission

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Abstract:

Conjugated polymers (CPs) have shown extreme promise in light-emitting devices due to their exceptional optoelectronic properties, low cost and solution processability [1]. However, the lifetime of any CP-based device is limited by the photo- and thermal instability of the CP [2]. Incorporation of CPs into an inorganic host provides an elegant route to modulate the optical properties and aggregation state of the CP [3], whilst improving the environmental stability. However, due to the chemical incompatibility of the two components, inhibiting phase separation across all length scales can be challenging [3]. To address this problem, we have investigated the potential of *di-ureasil* hybrids as a host material for CPs. Di-ureasils contain an organic polyether component grafted onto a siliceous network *via* two urea linkages which can be cast as thin films from solution. In the absence of a dopant species, di-ureasils are inherently photoluminescent and exhibit an excitation wavelength dependent emission band between 450-500 nm [4]. The aim of this work is to incorporate two red-emitting CPs, MEH-PPV and P3TMAHT, into the di-ureasil matrix, in an effort to improve their photochemical and thermal stability, whilst exploiting the potential for energy transfer between the di-ureasil and the CP to tune the emission properties. These CPs were introduced into the sol-gel mixture during the di-ureasil synthesis, which immobilises the CP within the host. Structural characterisation shows that incorporation of the CP leads to no significant structural disruption of the di-ureasil host. In addition, thermal analysis shows an increase in the thermal stability of the CPs within the di-ureasil host. Steady-state and picosecond time-resolved PL measurements were used to characterise the optical properties of the CP-di-ureasil hybrids and to probe the energy transfer dynamics between the host and the CP. Notably, the emission colour can be tuned across the blue-white-yellow spectral region by changing the excitation wavelength and concentration of CP. The tuneable nature, improved stability and processability of these materials make them a viable and intriguing prospect for use in solid-state white lighting.

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Arresting cell growth by novel indolocarbazoles functionalised by Lossen Rearrangement

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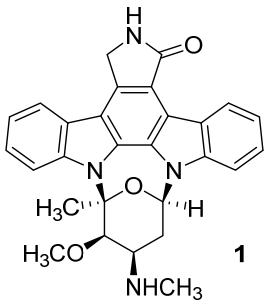

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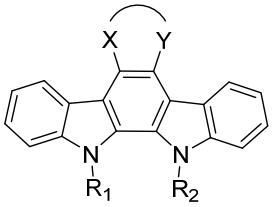

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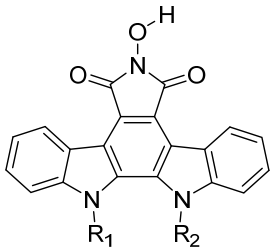

3

Abstract:

Cancer causes about 13% of all human deaths and at least one fifth of all deaths in Europe and North America [1]. Although chemotherapy is increasingly prescribed, it is not without side effects and so new, more selective remedies for cancer sufferers must be found.

Since the discovery of the anticancer properties of the indolocarbazole staurosporine **(1)**, many analogues have been synthesised in order to obtain compounds that have a higher potency with respect to anticancer mechanisms [2,3]. The overall objective of this project is to produce selective and highly potent novel anticancer agents through modification of the indolocarbazole structure **(2)**. Part of this work focusses on utilising a hydroxymaleimide as a replacement for the lactam/maleimide and forming a series of novel derivatives through substitution on the indole nitrogens **(3)**. These hydroxymaleimides can be modified via a Lossen rearrangement to form a series of novel substituted uracils. Biological evaluation via the NCI 60 cell line screen has been completed for a number of these compounds with some showing significant selectivity towards individual leukaemia and melanoma cell lines.

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Chain transfer to solvent in the radical polymerization of *tert*-butylacrylamide

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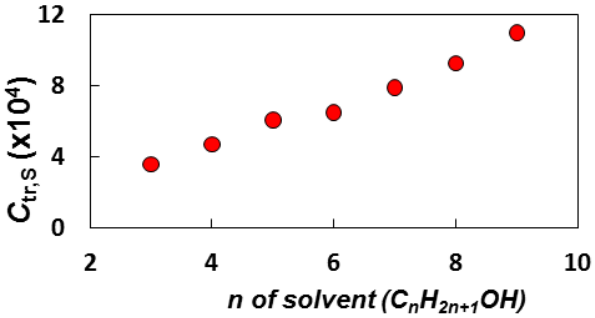

Figure 1. $C_{tr,S}$ is plotted versus the number of carbons (n) in linear alcohols. Chain transfer to solvent constant ($C_{tr,S}$) was estimated using Mayo plots at 120 °C.

Abstract:

Chain transfer to solvent is the abstraction of a hydrogen atom by a propagating radical to give a dead polymer chain and a solvent radical capable of initiating a new chain. Chain transfer to solvent in the conventional radical polymerization of *N-tert*-butyl acrylamide (TBAM) in a range of alcohol solvents is described [1]. Mayo analysis of polymerizations of TBAM in linear alcohols (C_3-C_9) resulted in approximately linear increase in chain transfer to solvent constant ($C_{tr,S}$) with the number of methylene (CH_2) units in the solvent (Figure 1).

The branched alcohol 3-methyl-3-pentanol gave the smallest $C_{tr,S}$ (using Mayo analysis at 120 °C) and thus allowed attainment of higher molecular weights in the nitroxide-mediated polymerization (NMP) of TBAM at 120 °C. 3-Methyl-3-pentanol, the solvent with the fewest CH_2s is thus recommended for solution NMP and other controlled/living polymerizations, where molecular weight growth is limited by chain transfer to solvent.

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An experimental study of isobutene ignition delay time at elevated pressures

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Abstract:

Isobutene is an important intermediate in the pyrolysis and oxidation of branched alkanes such as isobutane, isopentane and iso-octane. In addition, the oxidation of methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE), which are used as octane enhancers, also produce significant quantities of isobutene. Thus, well-validated detailed chemical kinetic mechanism to describe the oxidation of isobutene is important in order to build accurate chemical kinetic models for larger species. Despite these importance, there is a lack of experimental data available in the literature for isobutene at low and intermediate temperatures (700-1200 K) and at high pressures (≥ 10 atm)

In this study, rapid compression machine (RCM) and shock tube (ST) ignition delay time measurements have been made for isobutene fuel/air mixtures at equivalence ratios of 0.3, 0.5, 1.0, and 2.0. The wide range of experimental conditions included temperatures from 760 to 1500 K at pressures of approximately 10, 30, and 50 atm. Moreover, the ignition delay time of another 2 butene isomers (1-butene and trans-2-butene) was measured on shock tube under the same conditions as well in order to investigate the fuel structure effect.

The results for isobutene ignition delay time measurements show that, for several pressures and equivalence ratios, the ST and RCM results are in excellent agreement. NTC behavior was not observed for isobutene oxidation at any of the conditions studied. As to the effect of pressure on ignition, it is apparent that reactivity increases with increasing pressure. Moreover, at these particularly high-pressure (30 and 50 atm) and relatively low-temperature conditions (≤ 950 K), fuel-rich mixtures are most reactive while fuel-lean mixtures are slowest to ignite. Furthermore, at relatively high temperature conditions (≥ 1000 K), there appears to be a lesser dependence of ignition delay time with equivalence ratio. Moreover, at 10 atm pressure and relatively high temperature conditions (≥ 1100 K), there appears to be no dependence on equivalence ratio with all mixtures igniting at about the same time at the same temperature and pressure. As to the effect of fuel structure, 1-butene is the easiest to ignite, followed by trans-2-butene, with isobutene being the slowest. These experimental results will be used to validate detailed chemical kinetic models for both fuels.

References:

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Synthesis of α-glycolipids based on triazoles via α-glycosyl azides

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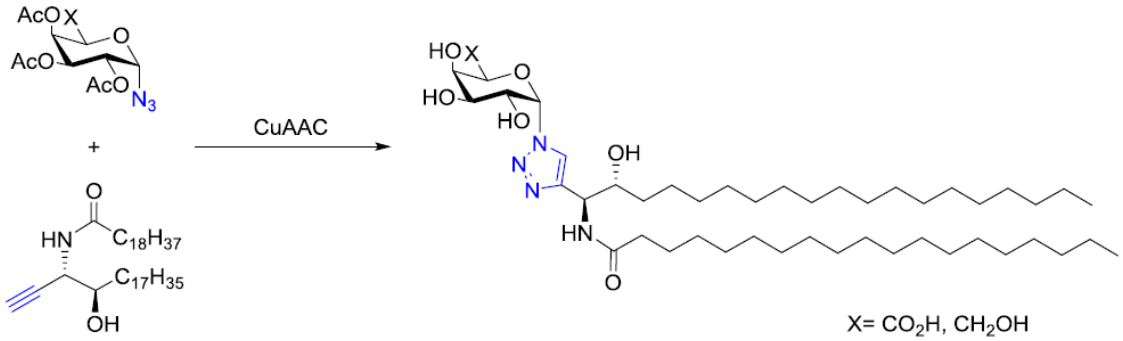

Abstract:

Glycolipids which are structurally related to KRN7000 and produced by *Sphingomonas* bacteria play an important role as antigens for natural killer T (NKT) cells to release cytokines [1]. Stimulation of NKT cells is achieved *via* presentation of glycolipids by the glycoprotein CD1d [2]. A limited number of glycolipids have been identified to stimulate NKT cells. Thus, novel strategies for the synthesis of new glycolipids antigens have been developed. Structural modifications include: Substitution and variation of the sugar, modification of the polar moiety of the ceramide, the lipid chain and the nature and configuration of the glycosidic bond.

Presented here are the syntheses of two 1,4-α-triazole glycolipids based on galactose and galacturonic acid [3]. Key steps include chelation induced anomerisation to provide the α-azide precursor and copper azide-alkyne cycloaddition (CuAAC) achieve the desired triazoles [4].

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Anomerization and anomeric effect in uronic acids

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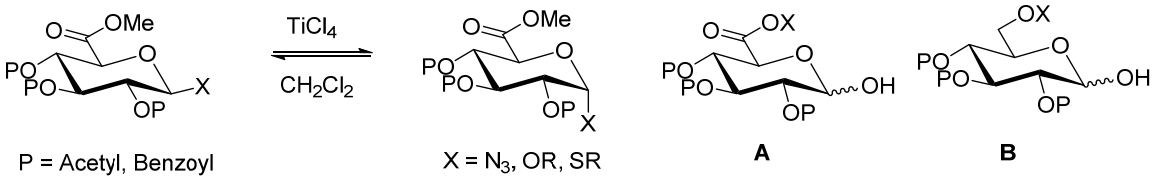

Abstract:

1,2-cis-glycosyl residues often form components of a wide variety of natural glycosides, many of which display significant biological roles and therapeutic potential. Synthesis approaches can be compromised when it comes to preparing 1,2-cis glycosides and some give a mixture of anomers [1].

The Murphy group have synthesized α-glycosides, particularly glucuronides and galacturonides through the use of a chelation induced anomerization [2,3]. High α-selectivites are possible, particularly for uronic acids, which could be due to a stronger anomeric effect in such saccharide derivatives. This highly stereoselective method is an accessible, direct route to the corresponding 1,2-cis glycoside, and if developed further could possibly be used to convert 1,2-trans glycosides to 1,2-cis glycosides.

The synthesis of a range of hemi acetals of glucuronic acids **A** will be presented and the anomeric effects in such compounds (α:β ratios) will be discussed and compared with corresponding glucosides **B**. Attempts to correlate this data with stereoselectivities obtained in chelation induced anomerisation reactions will be presented.

Acknowledgment: The authors are grateful to Science Foundation Ireland for funding (Grant No. 12/IA/1398).

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Towards a metal-based catalyst capable of the cleavage of the RNA component of human telomerase

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Abstract:

Telomeres are sections of non-coding DNA found at the end of chromosomes. They play a vital role in the life cycle of the cell as the length of the telomere acts as a mitotic clock which counts down the number of cell divisions a healthy cell can undergo before apoptosis occurs. DNA polymerase is unable to successfully replicate the ends of linear DNA strands and as such the chromosome loses 50-200 base pairs per mitotic division [1]. Once a critical length has been reached in normal, healthy cells, cellular senescence occurs. Chromosome ends are maintained by the enzyme telomerase which is composed of a protein (hTERT) and RNA (hTR) subunit. Expression of telomerase in cells leads to limitless replicative potential, one of the seven hallmarks of cancer. Telomerase represents an attractive target in the design of therapeutic agents due to its high incidence of occurrence in cancer cells and relative non-expression in normal cells. By synthesizing a drug with high selectivity for either component of telomerase, cytotoxic effects on healthy tissue can be addressed.

In this project, we seek to tether a metal catalyst *via* a linker moiety to a modified thymidine nucleotide and insert the catalytic moiety into a DNA/LNA mixmer. A mixmer has been selected as the targeting unit in this project as LNA has demonstrated a wide variety of attractive chemical properties conducive to the design of a successful antisense agent. Simply by adding a methylene linker between the 2'-oxygen and the 4'-carbon of the ribose unit, increased duplex stability, increased mismatch discrimination, increased selectivity, increased metabolic stability and lower toxicity has been achieved relative to unmodified DNA [2].

Kinetic studies on model compounds have been carried out on the free catalyst and on the catalyst linked to the modified thymidine moiety. Future work includes the tethering of the catalyst to the ribose unit of a suitably modified thymidine nucleotide and insertion of the catalyst into an oligonucleotide strand containing both DNA and LNA nucleobases.

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Lanthanide driven synthesis of novel luminescent self-assembly molecules and materials

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Abstract:

The aim of this research project includes three different functionalisations of the pyridyl moiety of the 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) containing ligand for lanthanide self-assembly and sensitisation of its luminescence [1]. A methyl ester (**1**) and, separately, an aromatic amine (**2**) were introduced on the 4-position. The methyl ester was further functionalised to the carboxylic acid derivative (**3**). A crystal structure of the Eu(**1**)$_3$.[CF_3SO_3]$_3$ was obtained and the photophysical properties of the ligand were analysed describing the self-assembly with Eu^{III} metal ions. The changes in the spectroscopic titrations were successfully fitted to the following equilibria: Eu^{III}+**1** $\rightleftharpoons$ Eu**1**, (log $\beta_{1:1}$=7.3 ± 0.4) and Eu^{III}+3 **1** $\rightleftharpoons$ Eu(**1**)$_3$, (log$\beta_{1:3}$ = 21.1 ± 0.7). The lifetime studies of these self-assemblies were recorded and, from this, the hydration state values were determined confirming the formation of fully saturated coordination sphere around the Eu^{III} ion (coordination number=9). This corresponds to the acquired structural data. Also, this opens up a whole new library of btp motifs with a possibility of 4-pyridyl substituents as 'handles' with which new functional groups can be introduced, and as such, the spectroscopic properties can be tuned.[3] Orthogonality of the positions Y and Z can be exploited for selective hydrolysis ensuring complete control over the potential self-assembly architectures possible. A benzyl ester in the para position is being developed for the purpose of selectively hydrogenating the ligand giving the para carboxylic derivative, thus, opening up avenues for further Ln(III) coordination, including the development of metal organic frameworks and self-assembly gels.

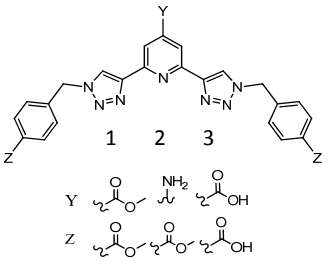

Figure 1 – Btp ligand with 4-substituted moities

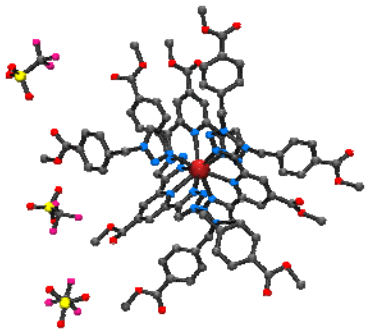

Figure 2 – Crystal structure of Eu(**1**)$_3$·[CF_3SO_3]$_3$

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