Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

School of Chemistry

Senior Sophister Projects for Chemistry 2021/22

Contents

Inorganic and Synthetic Materials Chemistry

New approaches to WEEE recycling: perfluorinated ligands for lanthanide extraction

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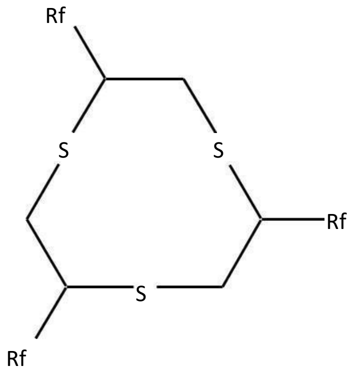
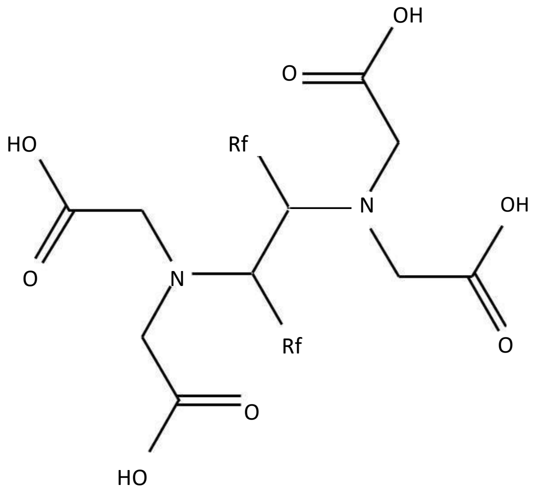
Research Project Description:

Lanthanide ions have been incorporated in an increasing number of technologies due to their unique properties. For example, neodymium is one of the key metals for magnets that are used in applications from wind turbines to hard disc drives. However, the amount of Nd that can be mined from the earth is not enough to continue the expansion of these technologies. This has lead the US, UN and EU to define the lanthanides as “energy critical”.[1] If the toxic metals and high value speciality metals could be separated, a sustainable recycling scheme could be implemented ensuring a ‘closed loop’ system for material use. This idea has recently been highlighted by a UN report that showed that recycling of such electronic equipment is not currently addressed in most developed countries. We have recently designed a number of highly fluorinated ligands for the extraction of toxic metals such as arsenic, tin or mercury or radionuclides such as uranium or plutonium.[2] The advantages of fluorinated ligands is that the ligands and metal complexes are soluble in supercritical carbon dioxide – an excellent solvent for “green” solvent extractions.

In this project you will synthesise a series of perfluorinated ligands and use them to extract the lanthanides europium and neodymium and monitor the extraction using UV-vis and emission spectroscopy. The initial aim of the project is to prepare one of the ligands below and fully characterize it using multinuclear NMR (^{1}H, ^{13}C, ^{19}F) spectroscopy and vibrational spectroscopy.





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3D printing for catalysis

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Research Project Description:

Immobilising of heterogeneous catalysts is an important topic as it allows the benefits of selectivity with the ability to separate products from the catalyst. With the advent of 3D printing, some work has shown that heterogeneous catalysts can be printed [1], but there are no reports of a homogeneous catalyst being incorporated into 3D printed 'reactionware'. In this project the aim is to immobilise a test catalyst – Wilkinsons Catalyst – into polycaprolactone that can be converted into filament for 3D printing. The advantages are that with the correct choice of polymer, the printing temperature will not decompose the catalyst; any shape reactionware module can be prepared; the reaction is on the solid-liquid interface, so this lends itself to microfluidics approaches where conventional techniques give high catalyst degradation and is the overall goal of this work.

The student will:

- prepare the catalyst,
- dope it into the polymer,
- convert this to a filament using in house equipment.
- Print reactionware using a 3D printer available for this project.
- Conduct test hydrosilylation reactions to evaluate the stability and recyclability of the catalyst.

In each step the catalyst will be characterised by solid-state ^{31}P NMR and thermal methods to ensure no oxidation or thermal decomposition of the catalyst. Wilkinsons catalyst is thermally stable to temperatures above the glass transition point of the polymer and has a convenient NMR probe. Once printed the catalyst will be used in the hydrosilylation reaction to evaluate the recyclability of the product and NMR spectroscopy will be used to see if the catalyst is leaching from the polymer.

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Non-innocent ligands for f-block chemistry

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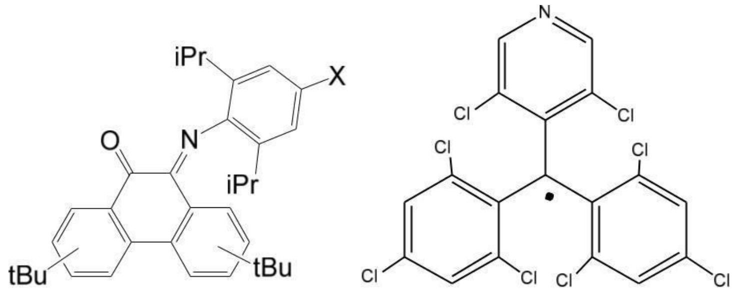
Research Project Description:
The lanthanide ions show intriguing magnetic properties that are only now being fully utilized. In contrast those properties of the actinides are very poorly understood.[1] We have reported on some unusual magnetism and spectroscopic properties of uranium(IV) but wish to expand our studies[2] into ligands that are non-innocent. In this case the ligand can contain one electron that can couple between two metal centers. In this project you will synthesise some ligands based on a semiquinone or aryl[3] type ligand system and explore the coordination chemistry to a number of transition metal and lanthanide complexes.



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Compound Interest: Heavy Metal Complexes as Photosensitisers

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Research Project Description: In general, the conversion of energy from one form to another flows downhill, with each step representing an energy loss. Upconversion is a mechanism by which carefully designed molecules can buck this trend by taking in light energy and pooling it so as to emit light of higher energy. This is a valuable phenomenon particularly in the development of next generation solar cells and photovoltaic devices and it has application in photocatalysis and luminescent oxygen sensing. The Draper team have uncovered the potential of some of their systems to engage in triplet-triplet annihilation, the molecular process at the heart of upconversion.[1]

Triplet-triplet annihilation (TTA) works by taking a sensitiser (usually a transition metal complex (Ru(II), Pt(II) or Ir(III)) with accessible triplet excited states) to harvest the exciting light and to transfer the energy by triplet-triplet energy transfer (TTET) to an acceptor. The triplet excited state is annihilated by the collision of two molecules to generate one in the ground state and one in its singlet excited state. The radiative relaxation of the latter produces the upconverted fluorescence. Our work has centred on a series of symmetrical Ir(III) and Ru(II) 1,10-phenanthroline complexes (Figure 1) incorporating aryl acetylene chromophores of increasing size.

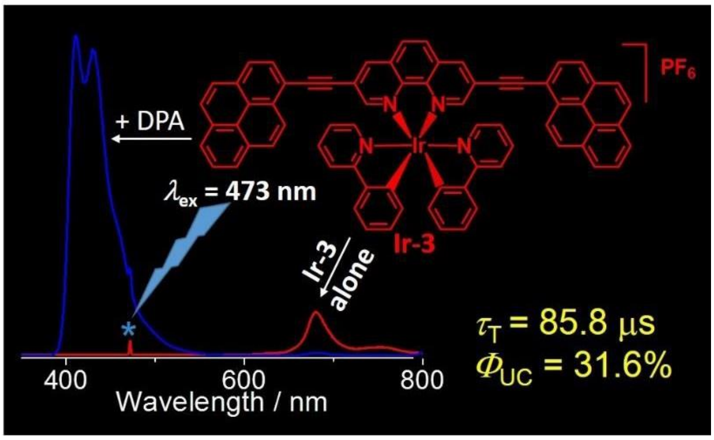

Figure 1: Emission spectra showing the sensitizer emission alone (red) and upconverted emission from DPA (blue) in a donor acceptor mixture (*exciting at 473 nm)

The aim of this project is to build on what is already known and to improve on these features in the next generation of triplet sensitizers.[2,3] The work forms part of on-going collaboration with Prof. Jianzhang Zhao's research group at Dalian University of Technology. To date it has yielded some of the highest known upconversion quantum yields.

The project will involve ligand design and synthesis and the spectroscopic characterisation of the resulting novel metal coordination complexes. The materials will be screened in TCD for their optical properties and lead compounds will be sent to China for further testing with the hope of making further new contributions to the applications of the materials in Photodynamic Therapy and chemical transformations.

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When it Glows: Hybrid Coordination Complexes with Photoluminescent Functionalities

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Research Project Description: Coordination polymers with two kinds of connectors are of great interest owing to their various potential applications.[1] Work within the Draper team has allowed for the formation of supramolecular coordination polymers using polypyridyl frameworks incorporating Cd(II), Sm(II), Ru(II), Fe(II) and heterometallic polymers based on Ag(I) and Ru(II). The research undertaken demonstrates the potential for -stacking interactions to influence the crystal packing and supramolecular ordering in the solid-state. In a parallel research programme the Draper team has established a versatile route to fused luminescent poly(heteroaromatic)graphenes and polyphenylenes.[2] The aim now is to connect these two areas of research to produce novel heterometallic coordination polymers with intriguing and potentially exploitable photophysical properties.

Research Project: Coordination polymers derived from photoluminescent lanthanide(Ln) metal ions (Eu(III), Tb(III), Nd(III) etc.) show luminescence in the NIR region, which has a special significance in the area of sensors.[3] Thus, binding the photoactive ML-fragment to Ln-based backbones in the proposed coordination polymers is expected to initiate definite changes due to energy transfer from the ML-fragment to the Ln-backbone. The plan is to prepare **novel** coordination complexes and coordination polymers with heterometallic centres based a series of proposed ligands and to investigate the material properties of the emerging supramolecular array. The target is a set of fused polypyridyl materials with low lying ▯-orbitals for near-IR absorption characteristics incorporating carboxyl groups for H-bonding interactions.

Methods/techniques: Synthetic activities will be undertaken within the host research laboratory and via the embedding of the student within the team. Metalloligands and coordination polymers will be characterized using various analytical techniques such as UV/vis absorption and emission spectroscopy, NMR, IR, ES-MS, and single crystal X-ray diffraction.

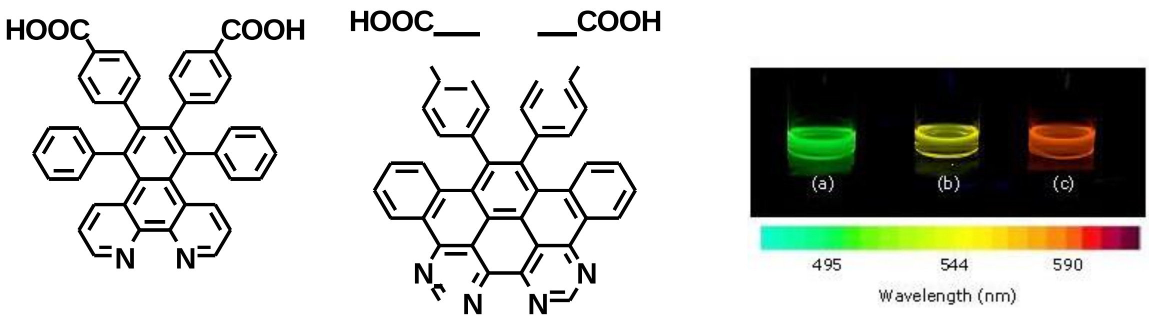

Figure 1 Proposed Ligands for generation of metal-based photoluminescent polymers

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Metal-based Molecular Switches Generated from Dithienyl Ethene (DTE)

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In recent years there has been a surge of interest in developing molecules that convert reversibly from one form to another on excitation with light.[1] This is because when the forms of a photochromic material have different properties (e.g. fluorescence intensity, absorbance profiles) they can be exploited as "On" or "Off" states in a molecular memory, data storage or switching device.

Dithienylethenes (DTEs), first described by Irie[2] and co-workers in 2000, have emerged as an important class of molecular switch, converting between open and closed forms (Figure 1). Most investigated are those comprising two 2,5-disubstituted thiophene units linked by a cyclopentene-derived bridge as these demonstrate high, thermal stabilities, fatigue resistance and cyclisation quantum yields.

Objectives: The concept of introducing a metal centre into the DTE motif is relatively recent.[3] Our intention in this project is to contribute to this emerging field and to use metal coordination as an effective tool to lock certain organic conformations in place and to tap into metal-based states that will facilitate cyclisation via a different electronic pathway than that adopted by a purely organic material.

The group[3] is currently working with Prof. F. Scandola an expert in the field and the project will involve organic synthesis, metal coordination chemistry, various characterisation tools, UV/Vis absorption and emission data and electrochemistry.

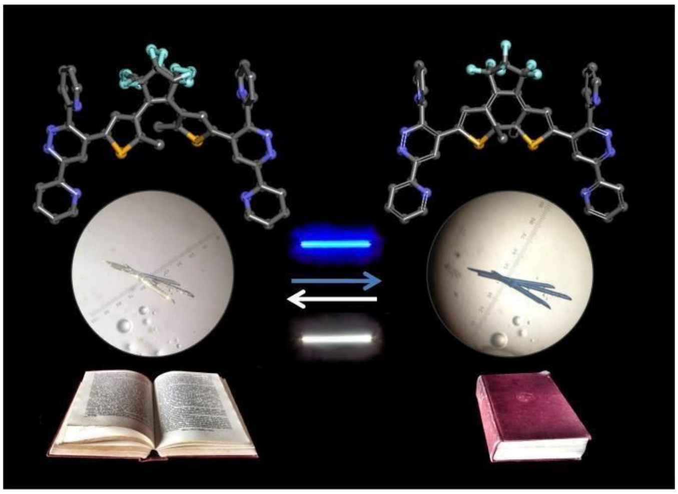

Figure 1: The Open (colourless) and Closed (blue) of crystals of a novel molecular switch

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A Molecular Approach to Heteroatom-Nanographenes: tuning electronic behaviour with a synthetic chemist's toolbox

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Products based on active thin-film organic devices are already in the market place e.g. as displays in mobile electronic appliances, however the future promises a radically new generation of ultra low-cost, lightweight, and flexible electronic devices if a carbon-based platform that can boast the necessary and discrete set of desirable properties and be found. Globally, there is a growing belief that graphene, the chemical focus of this project and heralded as the new material of the 21st century, could provide an answer to the emerging, translational and enabling nanotechnologies needed to replace silicon in the semiconductor industry. The problem is the absence of a band-gap in the pristine material.

Heteroatom doping is a promising approach for tuning the electronic properties of graphene, however current deposition methods for producing N-doped graphenes are unspecific (e.g. thermal evaporation of small organic moieties such as ethene and a nitrogen source (NH_3))[1] giving little or no control of the position or % of the N-atom dopants (Figure 1 (a)).[2]

This project aims to address this deficit by developing a controlled and strategic approach to the deposition of fully characterized heteroatom graphene-like materials. This will be achieved using the N, S and P-doped polyphenylenes developed in the Draper team[3,4] as feedstock. The work, facilitated by new and exciting collaborations between national and international groups, will allow a systematic and connected study of both solution and on-surface graphene development for the first time.

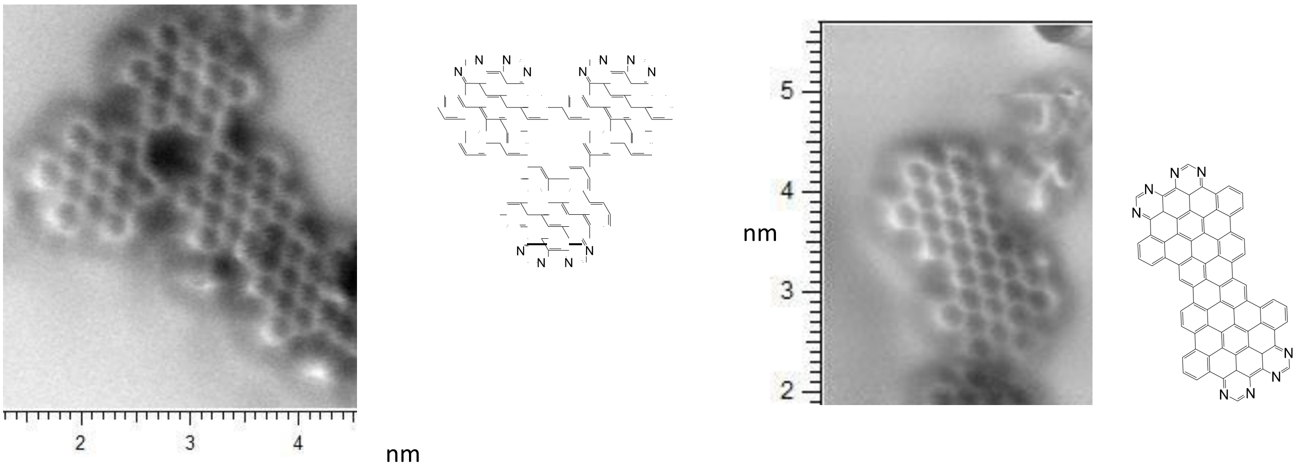

Figure 1 (a) Generation of N-doped graphene dimers via the thermal evaporation of precursors on Au (III) – Collaborator Prof. S. Decurtins

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School of Chemistry Senior Sophister Research Project 2021

Organometallic Polyaromatic Hydrocarbons

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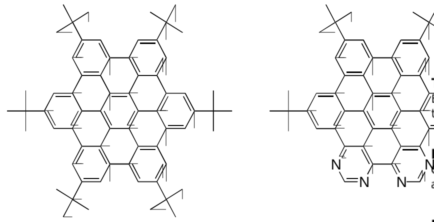
Research Project Description:

Polycyclic aromatic hydrocarbons (PAHs) are important materials and by-products from the burning of carbonaceous fuels. Carbenoid examples include anthracene and pyrene and larger coronene systems such as hexa-*peri*-hexabenzocoronenes **1** (Figure 1), (HBCs). Their coordination chemistry can be explored by incorporating heteroatoms into their periphery (**2**)[1,2] but they also have untapped potential as organo-ligands and very few have been used to incorporate -bonded metal centres. The aim of this project is to generate a new set of metal-organics with interesting and tunable photophysical and chemical properties. Such compounds are molecular models of metal-intercalated graphitic sheets and commonly used catalysts, such as dispersed Pd on graphite.



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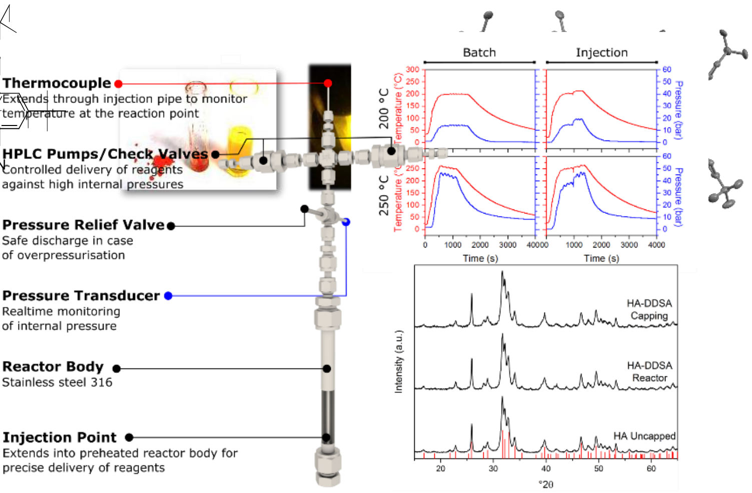

Figure 1: Planar (1), heteroatom-doped (2) and twisted (3) derivatives of HBCs synthesised in the Draper team.

Interestingly although large polycyclics incorporating up to 222 carbon atoms have been characterised, very few include an organometallic moiety[3] and there are only three examples of a metal π-complex of **1** (one is illustrated in Figure 2). There is even less work on twisted aromatics (**3**) where the electronic platform is less delocalised and potentially more reactive.

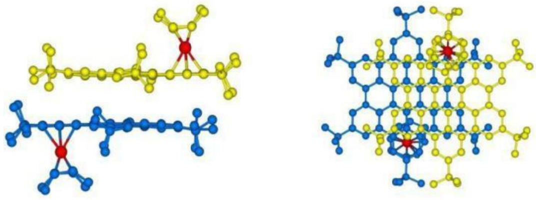

Figure 2: Molecular structure via single crystal X-ray diffraction of [(C8H12)Rh(h^{6}-1][BAr^{F}4]. Showing dimeric-stacking of molecules. H atoms and counter anion not shown

Having prepared the organometallic counterparts of these systems it is possible to determine – how the HOMO-LUMO gap varies on coordination and influences electron transfer from metal centre to aromatic plane. The integration of this type of information is important for establishing its structure/property characteristics and opto-electronic applications where alignment and stacking are very important.

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Hollow and Complex Metal Sulfide Microstructures Grown from Colloidal Sulfur Seeds

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Research Project Description: The formation of complex, biomimetic structures from ostensibly simple inorganic systems has been a source of fascination for centuries. This is exemplified by chemical gardens, in which non-equilibrium precipitation processes result in complex, plan-like micro- and nanotubular morphologies driven by diffusion, osmosis, and convection effects.[1] Such systems have seen a recent resurgence in interest, as the hollow structures obtained are envisaged as likely adsorbents, catalysts, sensors and fuel cell components.[2] In addition to these potential applications, similar complex biomimetic structures have also been identified as potential biomarkers indicative of primitive life both on earth, and further afield. It is thus important to explore potential abiotic routes to these structures to confirm or disprove their role as biosignatures.[3]

We have recently developed a simple route to hollow, framboidal, and plant-like copper sulfide, grown from colloidal sulfur seeds. By reacting these sulfur colloids with a copper salt solution a range of morphologies may be achieved. Based on investigation of these products by powder X-ray diffraction and SEM it is posited that each of these varied and complex morphologies is the result of a nominally simple process analogous to that observed in the freezing of water droplets. Here we aim to expand this approach to a more generally applicable route to hollow and complex metal sulfide microparticles including ZnS and CdS.

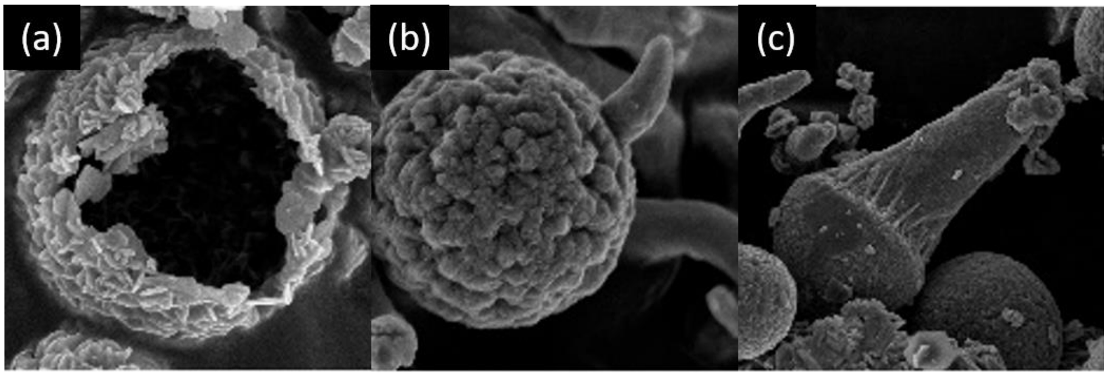

Figure 1: Copper sulfide microstructures grown from colloidal sulfur seeds; (a) hollow microsphere, (b) budding sphere, (c) grown tendril.

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Green Synthesis of Inorganic Nanomaterials by Hydrothermal Injection

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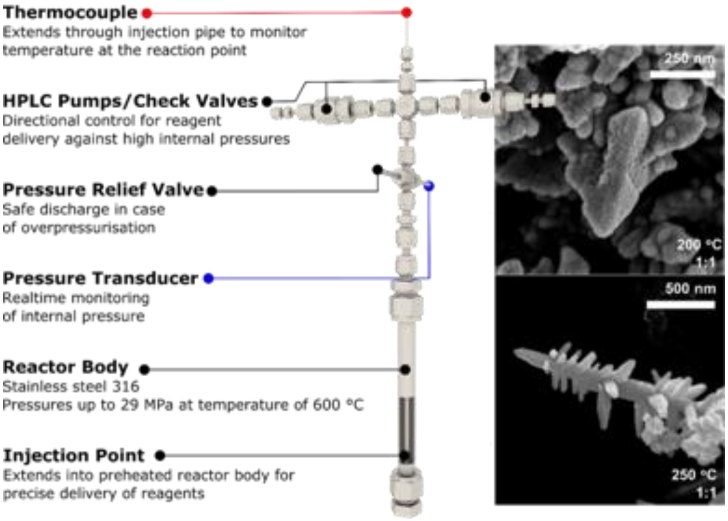
Research Project Description: The properties of inorganic nanomaterials are highly dependant on their crystalline phase, size, shape, and surface chemistry.[1] Synthetic methods to control these properties are thus highly important. The well-established hot-injection process is among the most widely used methods for the size, phase and shape-controlled synthesis of inorganic nanomaterials, however a major drawback of this process is the requirement for environmentally costly high boiling point organic solvents and often toxic organometallic precursors. Here we will use a newly developed hydrothermal injection process to produce functional inorganic nanomaterials using only water as a solvent. This project will target the synthesis of zinc and cadmium sulfide quantum dots; surface modified hybrid organic-inorganic nanomaterials with size-dependent optoelectronic properties. Prior work on the hydrothermal injection system has shown that these materials, which exhibit cubic-hexagonal polymorphism, may be selectively nucleated and grown in a particular phase, based on reaction conditions (see figure below).[2, 3] Here we will expand this work to include surface modifying agents to further control particle size and surface chemistry. It is expected that this project will help develop the hydrothermal injection technique as a green route to functional inorganic nanomaterials. The student will gain experience in materials synthesis and characterisation techniques, such as powder X-ray diffraction and electron microscopy.



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School of Chemistry Senior Sophister Research Project 2021

Synthesis and Characterisation of Magnetic Nanomaterials

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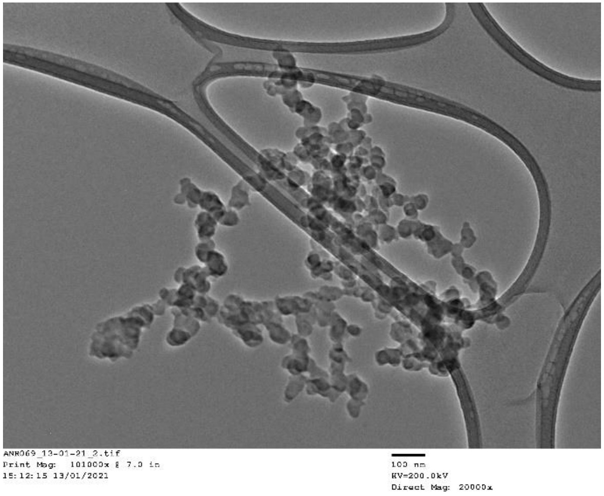
Research Project Description: Magnetic nanomaterials, such as simple iron oxide and the more complex ferrites, $M^{II}Fe_2O_4$, are hugely important functional materials due to their applications in data storage, biomedical imaging, catalysis and separation. The properties and subsequent applications of these materials are dependant not only on their composition, but also their size, shape, monodispersity, and surface functionalisation. Key to achieving control of these parameters is the separation of nucleation and growth processes. This has most successfully been accomplished by thermolysis or hot injection, whereby precursors are introduced into a high boiling point organic solvent, inducing a rapid burst of nucleation to generate uniform nanoparticles.[1, 2] While these approaches have proven to be highly versatile and successful, they require hazardous, petrochemically derived high-boiling point organic solvents and often uses toxic organometallic precursors. Hydrothermal processing, which uses only pressurised, superheated water as a solvent, is thus an attractive alternative route to magnetic nanoparticles, as shown below.

Here we will compare conventional thermolysis/hot-injection routes to magnetic nanomaterials, employing air-free synthetic techniques, with hydrothermal and solvothermal methods. Products will be characterised by powder X-ray diffraction, electron microscopy, infrared spectroscopy, and thermogravimetric analysis. It is anticipated that this project will provide a path towards cleaner, greener routes to these key materials.



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New membranes for water purification

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Research Project Description:

Introduction

Water for both domestic and industrial use is becoming a scarce and expensive resource requiring careful control and protection. Membrane based separation systems dominate the European market for industrial process water treatment equipment. In particular, recently new nanotechnology-based solutions (nanofiltration) have emerged as potentially superior and cost-effective ways to remove sediments, charged particles, chemical effluents, bacteria and other pathogens in addition to the removal of toxins like arsenic or impurities like oil [1]. However, biofouling of membranes is a severe and common problem. The growth of biomass on the surface of membranes and adsorbents (biofouling) limits both the efficiency (volume treated per unit time) and lifetime of systems and necessitates periodical washing of the membrane equipment with aggressive chemicals. There is, therefore, a pressing need to develop antifouling systems that exhibit active durability and are eco-friendly.

Objectives

The main goal of this project is to develop new nanofiltration approaches and membranes for complex water purification. In this project, biofouling issues and other related problems will be addressed *via* development of a new generation of active membranes with potential anti-fouling properties which will be designed and engineered at low cost. The increasing safety of NMs is of particular importance and we will implement the necessary measures to prevent the occurrence of nanoparticles in treated water, using our membrane design in addition to filtering pre-existing particles from water. New membranes of varying compositions and porosity will be tested to determine the optimal water treatment conditions.

Expected outcomes

The successful realisation of this project will result in the development of new nanostructured adsorbents and membranes with enhanced bactericide and anti-biofouling activity, which will allow removal of various contaminants including bacteria, oils, grease, dyes, detergents, colloidal substances, toxins, pesticides, drugs and antibiotics from water. The special purity water will be particularly important for food industries in Ireland, for example for production of various drinks and dairy products. The exploitation of new membranes will give potential users more reliable, cost efficient treatment that generates high quality water, with a tailored mineral content.

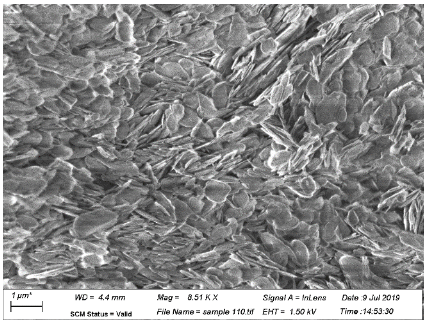

Figure: Cross-section scanning electron microscopy image of new membrane for water purification.

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New Luminescent Solar Cell Concentrators

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Research Project Description:

Introduction

Sunlight provides the largest of all carbon-neutral energy sources. The luminescent solar concentrators (LSCs) offer the opportunity to concentrate both diffuse and direct sunlight and have a number of important potential applications including: solar cells, integrated photovoltaics, smart windows, greenhouses, and glazing in buildings. LSC is in its simplest form is a slab waveguide, of usually rectangle dimensions as shown in Figure 1, designed to concentrate light incident on its top face to its edges [1, 2]. Normally LSCs involve the use of a photoluminescent dye-doped matrix, which firstly absorbs incident sunlight and reemits it in the form of fluorescence. These emitted photons radiate in all directions from the dye, with a certain portion of them being trapped by the LSC due to total internal reflection, which is dependent upon the refractive index of the matrix. Hence, due to the difference in surface area of LSC edges relative to its top surface, light is concentrated at the edges. Therefore, if a solar cell is then attached to the edges a large increase in the solar cell power is found to take place.

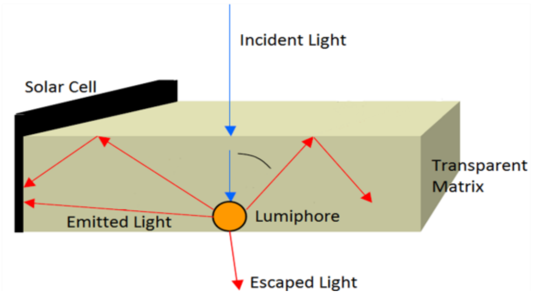

Figure 1. Basic design of a Luminescent Solar Concentrator (LSC).

Objectives

The main aim of the project is to develop new luminescent solar concentrators formed from transparent polymers (e.g. polymethylmethacrylate, PMMA) and non-toxic semiconducting nanocrystals, quantum dots (QDs). In this project we plan to use non-toxic QD based luminophores, that maintain the preferable photophysical aspects mentioned, while avoiding the pitfalls. The research work will include following technical tasks: (i) QD preparation and characterisation; (ii) new LSC design and fabrication; (iii) LSC-solar cell tandem prototyping and testing.

Expected outcomes

The successful realisation of this project will result in the development of new LSCs, which will then be integrated to a range of commercially available solar cells. A selected LSCs and photovoltaic cells will be tested including, monocrystalline and polycrystalline Si-based cells.

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Multimodal magnetic core-shell nanoparticles

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Research Project Description:

Introduction

Multimodal magnetic nanoparticles have been used for a broad range of applications including catalysis, cell labeling, drug delivery, hyperthermia treatment and biological imaging (e.g. see Figure below) [1, 2]. The focus of our research is the development of new magnetic nanostructures and their conjugates to be used as potential theranostic tools in cancer research. These structures possess the unique advantage of the large surface area and small size characteristic of nanoparticles, coupled with the magnetic modality required for biological imaging and drug delivery.

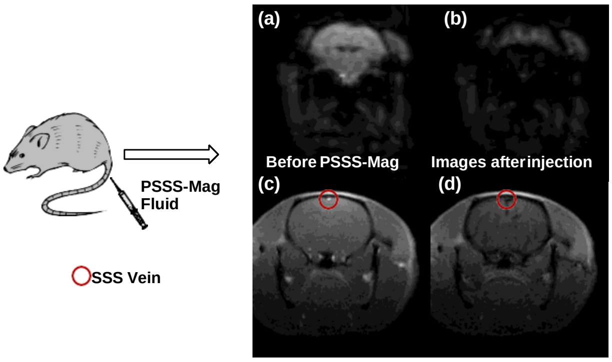

Figure: Echo planar image (EPI) of mouse brain (a) before and (b) as magnetite-based magnetic fluid passes through; Fast Low Angle Shot (FLASH) image of mouse brain (c) before and (d) as our new MRI fluid passes through.

Objectives

The main goal of this work is to develop new multimodal magnetic nanocomposites for biomedical (e.g. MR and CT imaging and cancer therapy) applications. Magnetic oxide core-shell nanostructures will be synthesised using co-precipitation and other processing techniques. The characterization testing and evaluation of new materials will be performed by electron microscopy, FTIR, Raman spectroscopy and magnetization measurements. The nanomaterials will be functionalised with specific biomarkers and drugs and will be tested for potential *in vitro* and *in vivo* cancer diagnostic and therapy.

Expected outcomes

The successful realisation of this project should result in the development of new multimodal magnetic nanomaterials, which could serve as MRI and CT contrast agents and vectors for drug delivery in cancer therapy.

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Mimicking Class Ib Dimanganese Ribonucleotide Reductases

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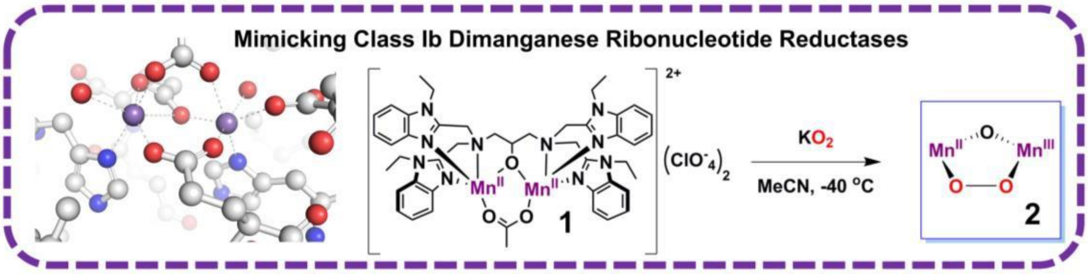
Research Project Description:
The research proposed herein will address the Chemistry of a family of enzymes that play a pivotal role in human health. You will perform a project in the area of Bioinorganic Chemistry. You will explore the natural Chemistry of a family of enzymes called Ribonucleotide Reductases (RNRs). RNRs employ dioxygen and manganese for the biosynthesis of deoxyribonucleotides, precursors to DNA.

You will attempt to gain an understanding of the mechanism and intermediates of the reactions these enzymes catalyse. This will help us to understand their biochemistry, and develop treatments where these metal-containing enzymes are performing adversely. You will develop synthetic small-molecule analogues of the active site of these enzymes. These small-molecule compounds will display the same physical properties as the enzymatic active site.

You will focus on a single aspect of the postulated reaction mechanism, that is the reaction of a derivative of dioxygen, called superoxide, with dimanganese (and other bimetallic) complexes. Superoxide interacts with the metal site in these enzymes producing a so-called metal-peroxide intermediate. You will synthesise metal-superoxide complexes and investigate their reactivity properties. In investigating these model compounds, we will probe the kinetics of these reactions, identify the products of reactions, and try to verify the postulated reaction mechanism for the RNRs. The outcome of these investigations will be particularly exciting, because it will provide the first and the only experimental investigations into certain biochemistries of this large family of metalloproteins. You will utilise organic and inorganic synthetic methods in this project, learn how to perform reactions under exclusively anaerobic conditions, as well as gaining skills in a variety of spectroscopic techniques.



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Adriana M. Magherusan, Ang Zhou, Erik R. Farquhar, Max García-Melchor, Brendan Twamley, Lawrence Que, Jr., Aidan R. McDonald*, *Angew. Chem. Int. Ed.* **2018**, *57*, 918-922

High-Valent Metal-Halide Oxidants

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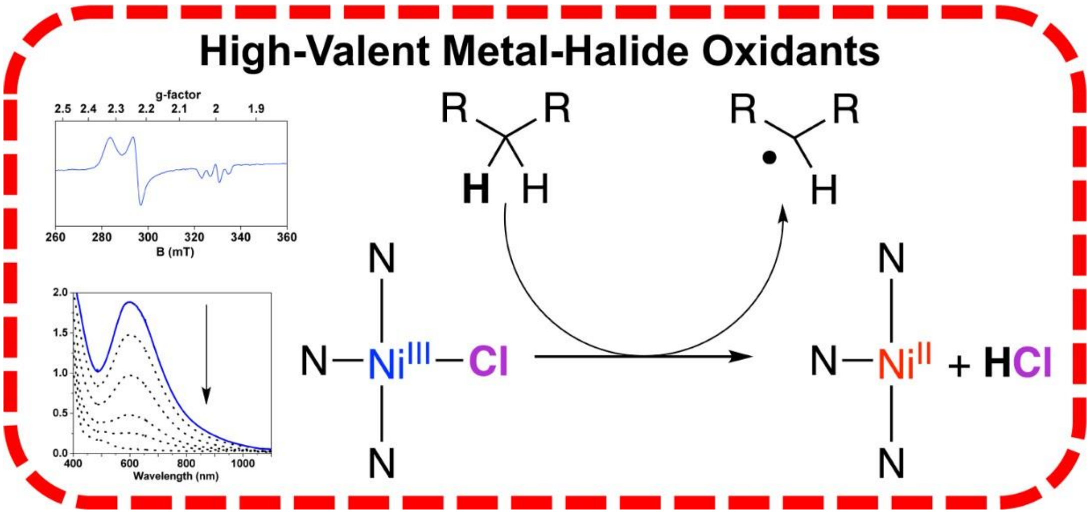
Research Project Description:

The oxidative functionalization of inert C–H bonds in hydrocarbons is an important transformation in biological systems as well as industrial catalysis. A large number of Fe- and Cu-containing metalloenzymes perform such hydrocarbon oxidations, forming hydroxylated, halogenated, or desaturated hydrocarbons. It has been proposed that such reactions involve hydrogen atom transfer (HAT) from an inert C–H bond to a high valent metal-based oxidants such as metal-oxo (M=O) and M-OX (OX = OH, OR, O_2C-R, ONO_2). However, the HAT reactivity of the metal-bound halide in C–H/O-H activation has rarely been studied, although we postulate there will be a very high driving force for such oxidations.

The major objective of this project will be to prepare a series of metal-halide (Ni, Cu) complexes supported by stable and robust ligands. You will prepare high-valent derivatives of these complexes and subsequently investigate the reactivity of the corresponding high valent metal halide complexes towards hydrocarbons. It will also be a goal to explore the oxidative halogenation of hydrocarbons using such compounds. You will utilise organic and inorganic synthetic methods in this project, learn how to perform reactions under exclusively anaerobic conditions, as well as gaining skills in a variety of spectroscopic techniques.



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Functionalisation of 2D Nanomaterials for Catalysis

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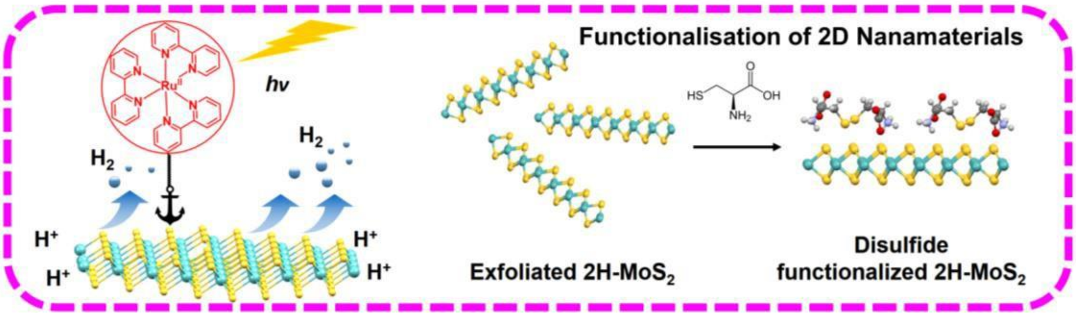
Research Project Description:
Molybdenum disulfide (MoS_2) is a widely used catalyst for important industrial processes like hydrodesulfurisation and hydrocracking of pertroleums (it is used to remove sulfur containing molecules from fuels, limiting emission of SO_2 gas). Furthermore, MoS_2 is a highly reactive hydrogen evolution catalyst. We explore the reactivity properties of two-dimensional (2D, analogous to graphene) MoS_2 nanosheets for applications in hydrodesulfurisation and hydrogen evolution catalysis. We expect exceptional enhancement in catalytic efficiency when moving from bulk MoS_2 to 2D MoS_2 nanosheets. We attribute this to the increase in S vacancy defects and Mo free sites present at the edges in the delaminated (2D) nanomaterials. These sites are known to facilitate adsorption of reactive molecules onto the catalyst surface, and therefore may enhance reaction rates.

This project will focus on the exploration of the reactivity properties of 2D MoS_2 (and functionalised derivatives thereof) in hydrodesulfurisation and hydrogen evolution reactions. You will prepare 2D MoS_2 nanomaterials, characterise them using an array of spectroscopic probes (UV-vis, FT-IR, TGA, XRD, XPS, Raman). You will then optimise the reactivity properties of the 2D nanomaterials.



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Self-assembly in Large Molecular Weight Block Copolymers for Nanopatterning Applications

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Research Project Description:

The self-assembly of large molecular weight block copolymers into spatially oriented nanodomains has opened up a range of new possibilities in the manufacture of sub-wavelength optical nanostructures, such as Si nanopillars for anti-reflective coatings [1]. In order to obtain such effects in the visible spectrum, the block copolymer domain sizes need to be greater than 100 nm. These have been synthesized thus far by our group using high molecular weight PS-*b*-P2VP block copolymer thin films on silicon substrates.

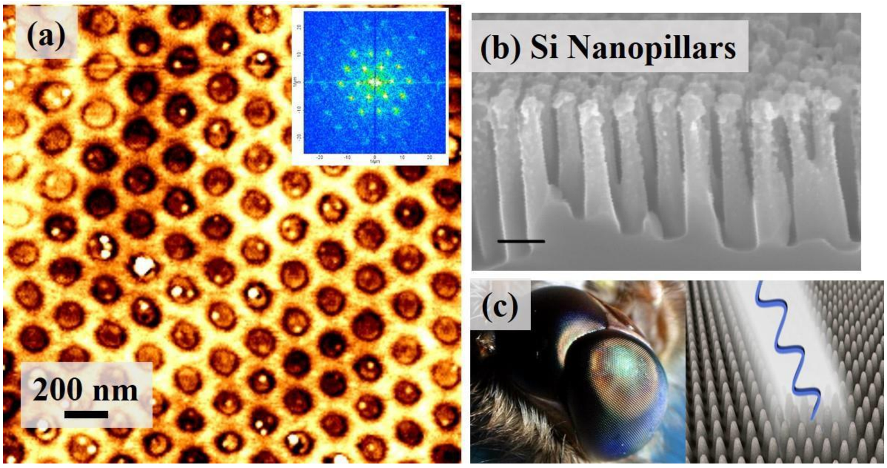

Figure 1. AFM topography image of (PS-*b*-P2VP), (b) Si Nanopillars synthesized using PS-b-P2VP as a mask mimicking moth eye (c).

This project will aim to expand on this work, examining the formation of domains using other molecular weights and families of block copolymers. Varying molecular weights of polystyrene-*b*-2-vinylpyridine (PS-*b*-P2VP) will be tested, along with high molecular weights of polystyrene-b-polyethylene oxide (PS-*b*-PEO). PS-*b*-PEO has shown strong potential for nanostructure fabrication, however the domain sizes thus far have remained below that required for optical applications in the visible spectrum [2]. The phase separation of high molecular weight block copolymers is little understood, and will need to be optimized for these new polymer systems. This will involve the fine-tuning of each process outlined below in the synthesis route – including the polymer solution concentration, phase separation process, and ethanol swelling. In terms of characterization, the feature spacing, film coverage, diameters and structural characteristics for each block copolymer will be examined and compared.

If successful, nanostructures will be generated using metal infiltration these onto silicon and glass substrates, which will be etched to produce nanoscale features. It is hoped that this work will lead to the formation of a variety of morphology and feature sizes, each of which could be utilized for different nanostructure applications.

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Large Area Nano-porous graphene Membranes Derived from self-assembled Block Copolymer Lithography

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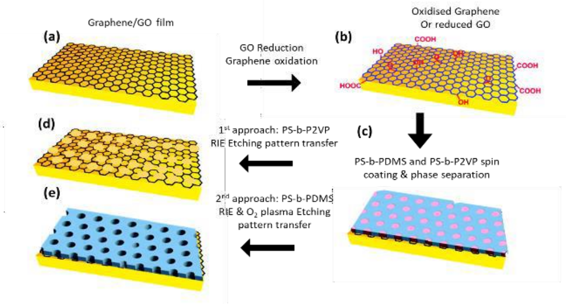
Research Project Description:

Highly selective and high-permeable membranes are the scope for the future separation technology to address the limitations of the current membrane technologies. An efficient membrane should compete in four main criteria: high selectivity, high permeability, mechanical integrity, and resistance to fouling. Two-dimensional (2D) materials are an ideal alternative for fabrication of ultrathin membrane which promises ultimate permeation. Among 2D materials, Graphene owing to chemical stability, and inherent impermeability offers a unique 2D membrane if perforated precisely[3]. Despite the fact that many researches has been conducted so far on generating nanopores on graphene using various techniques, yet there is a lack of efficient and reliable method to produce graphene membrane in large scale [3,4].

The aim of this project is precisely perforate graphene oxide and graphene nanosieve using a unique block copolymer nanopatterning method with up to 108 pores/cm2 of hexagonally ordered pores with uniform size and distance from less than 10 nm up to few 100 nm. Nanoporous graphene membranes derived from this method have tremendous promise to fulfil all four of those requirements due to their narrow pore size distributions (high selectivity), high porosity (high permeability), robustness and antifouling properties [5,6].

Two strategy will be employed to create nanopores on graphene using two different type of block copolymers (showed in schematic diagram) (PS)- block-poly(4-vinylpyridine) (PS-b-P4VP) (d) and polystyrene-block-poly(dimethylsiloxane) (PS-b-PDMS) (e)[5,7]. This method is based on periodic micro-phase separation of the two incompatible blocks at equilibrium conditions to lead the minimal free energy configurations. The nanostructures can then be used as masks for pattern transfer to graphene via Reactive Ion Etching (RIE) and oxygen plasma. This approach integrating large-area graphene film with block copolymer lithography is potentially advantageous in creating 2D atomically thin membranes with predefined pore size for efficient separation of specific molecules with desired size.

Figure 1. Schematic of fabrication technique



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Block-copolymer Templated Silicon Nanoporous Monolith Embedded with AuNPs: Application in Confined Space Photocatalysis

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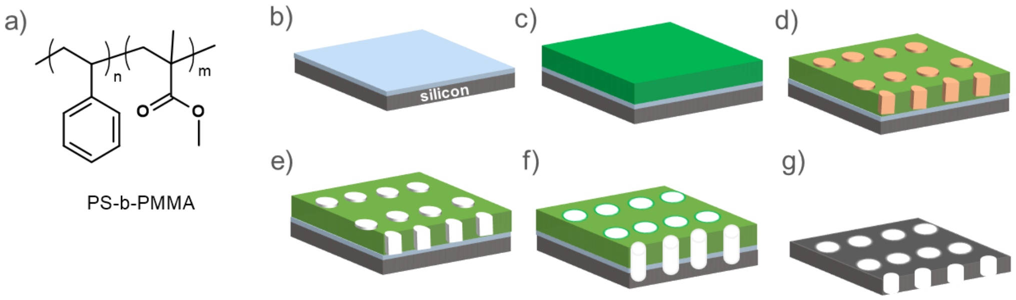
Research Project Description:

Metal nanoparticles are well known for their ability to produce large, localized electric fields. It has been observed that for multiple particles confined in nanostructured spaces, the enhancement of this near-field due to the plasmonic coupling is greater than for dispersed, isolated nanoparticles [1,2]. When the separation between nanoparticles is sufficiently small, the conduction electrons near each nanoparticle surface become delocalized and are shared between adjacent nanoparticles resulting in an electric field enhancement [2]. The plasmonic nanostructures with a tunable light-matter interaction have potential applications in efficient light harvesting applications such as photocatalysis, artificial photosynthesis, photovoltaics, water purification, and imaging and microscopy techniques, e.g., medical diagnostics.

The objective of this project is to study the effect of confinement plasmonicon photocatalysis.

Block-copolymer (BCP) soft-nanolithography is a versatile, robust, and cost-effective technique to nanostructure surfaces and produce a variety of surface morphologies such as nanopillars and nanocavities [3,4]. You will learn a new fabrication technique based on self-assembly of block-copolymers to produce nanostructured surfaces. During this research project we will employ poly(styrene)-block-poly(methyl methacrylate) (PS-*b*-PMMA) BCP (scheme 1) to define an etch mask for producing a nanoporous silicon substrate with gold nanoparticles embedded in it for photocatalytic applications. In the next step gold nanoparticles will be confined in nanopores. The advantages of this system are its high surface area, the ability to easily separate the photocatalytic monolith from the reaction system, and the close proximity of the metal nanostructures confined in the nanopores to couple plasmons efficiently. To investigate the activity of this platform, we will test different common pollutants such as dyes and their degradation under mild environmental conditions. We anticipate findings from this research will have potential applications in light harvesting energy materials and water purification.



Scheme 1: Schematic of the fabrication procedure of porous silicon substrate (a) Block-copolymer PS-b-PMMA, b) Deposition of brush copolymer, c) Deposition of block copolymer, d) Phase separation between PS and PMMA in vertically aligned cylindrical configuration, e) Selective chemical removal of PMMA, f) Plasma etch and pattern transfer to the Si substrate, and g) Removal of the mask residual.

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Study of the effect of water concentration on nitrocellulose membrane formation

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Nitrocellulose membranes are used in a range of applications ranging from bioassay through to separation and purification. The are commonly prepared by a processes of inverse phase separation where a solution of nitrocellulose (NC), acetone (solvent), water and other non-solvents is subject to a thermal or concentration change to cause polymer precipitation. The non-solvents act as pore formers to create the membrane structure. The pore size, pore volume and the appearance of the membrane is dependent on many parameters including water concentration. This project will seek to understand the relationship of membrane properties to water concentration be defining a phase diagram mapping morphology over a range of NC, solvent and non-solvent concentrations. We will extensively use light scattering to measure polymer aggregation and precipitation, microscopy to look at membrane morphology and quantify fundamental properties such as pore size, porosity and flow times.

Objectives:
a) To prepare NC by inverse phase inversion that have mean pore size of 2 - 15 um
b) To define the NC phase diagram as function of solvent and non-solvent concentration at a 14 – 16% NC concentration
c) To rationalise observations using solvent theories
Outcomes:
This work should contribute to publication of a journal paper. It should also help to define future manufacturing methods for NC production

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Growth of Novel CeO_2 films and their Surface Characterization

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Morrism2@tcd.ie

Short introduction:
Cerium dioxide, ceria or CeO_2 is one of the most used oxides in industry. It is the base material in a number of sensors and catalysts including air quality sensors, oxidation catalysts and the three-way automotive exhaust catalyst [1]. Its useful properties lie in its ability to cycle between CeO_2 and CeO_{2-x} without deleterious changes in structure or morphology. However, there remains controversies about its oxidation state and the redox mechanism. Particular concerns lie around the anion vacancy that is formed during reduction and how this can be properly characterized [2]. There has been recent work that suggests the anion vacancy is accompanied by the formation of O^- states rather than Ce^{3+}. Here we want to examine this phenomenon using x-ray photoelectron spectroscopy (XPS). We will use ceria thin films prepared by a new technique of polymer infusion recently developed in these laboratories [3]. Here, metal ions are incorporated into a polymer system which is then carefully oxidized to remove polymer and form a coherent oxide film. The prepared films will be characterized in depth by XPS and other techniques. Defect formation as a function of heating and surface treatment will be studied with a particular view of searching for surface O^- states.

Objectives:

a) To prepare ceria thin films by infusion technique that are homogenous and around 5 to 10nm thick.
b) Characterize films by XPS and advanced electron microscopy
c) To look at oxidation and reduction of thin films and delineate the role of anion defects in the formation of CeO_{2-x}.

Outcomes:
This work should contribute to publication of a journal paper. It should also help to define future work programmes in understanding the properties and stability of reduced forms of ceria.

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Towards Artificial Enzymes: Bio-inspired Oxidations in Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are important crystalline materials consisting of clusters or metal ions linked through organic ligands and resulting in microporous networks. MOFs are regarded as key compounds related to energy storage and conversion, as their unprecedented surface areas make them promising materials for gas storage and catalysis purposes. This project addresses the question of how MOFs whose functionalities may relate to those of biological enzymes can be constructed and exploited for sustainable energy, 'solar-fuel'-related applications. In order to design efficient oxidation catalysts, our proposed activities take inspiration from the oxygen-evolving complex (OEC) of photosystem II (PS-II) that catalyses the highly endergonic - H_2O oxidation half-equation to produce O_2. The energy demand of this latter reaction and the lack of cost-effective catalysts currently hampers the Technological breakthroughs towards sustainable H_2 economies. A scientific breakthrough would be one of the greatest scientific achievements with unprecedented impact to future generations. The Senior Sophister project will be assisted by a postgraduate/postdoctoral researcher and will involve the following key aspects:

a) **Synthesis and characterisation of organic ligands of new catalytically-active MOFs:** The student will synthesise new organic ligands which give rise to the formation of highly porous MOFs. The ligands will be reacted with a series of transition metal ions to form new MOFs whose building units resemble the active Mn site in PS-II. Depending on the project, ligands may comprise of light-harvesting ligands including polyaromatic carboxylates, porphyrins, etc. which will be synthesised in multi-step organic synthesis and characterised by NMR and IR spectroscopy.

b) **Structural and physico-chemical characterisation of the MOFs:** The X-ray structures, the thermal stability, the porosity and the surface area of the MOFs will be investigated.

c) **Investigation of the catalytic properties of the MOF:** The photo- and/or the electrocatalytic activity of the MOFs towards H_2O oxidation to produce O_2 or the formation of H_2 will be investigated.

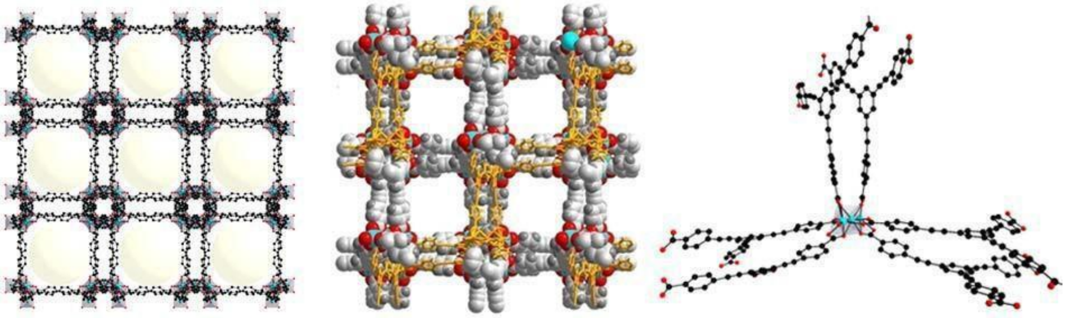

Figure: Crystal structure of a novel MOF that gives rise to porosity and ultra-high surface areas and high catalytic activity for the oxidation of H_2O.

Representative Publications:

(•) ***Nature Communications***, **2017**, DOI:10.1038/ncomms15268. *"Ultra-large supramolecular coordination cages composed of endohedral Archimedean and Platonic bodies"* (•) ***Eur. J. Inorg. Chem***, **2018**, DOI:10.1002/ejic.201800217. *"CO_2 Adsorption in SIFSIX-14-Cu-i: High Performance, Inflected Isotherms, and Water-Triggered Release via Reversible Structural Transformation".* (•) ***Chem. Commun.***, **2015**, *51*, 13313-13316, *"Towards multifunctional lanthanide-based metal–organic frameworks".* (•) ***Chem.- Eur. J.* 2014**, DOI: 10.1002/chem.201304856. *"Hetero-Epitaxial Approach by Using Labile Coordination Sites to Prepare Catenated Metal–Organic Frameworks with High Surface Areas"*

School of Chemistry Senior Sophister Research Project 2021

Supramolecular Coordination Cages for Bio-Inspired Catalysis and Bio-Medical Applications

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Coordination cages represent metallo-supramolecular species in which metal ions or small polynuclear complexes are connected through organic ligands to produce compounds with well-defined cavities. Over the last decades, extensive synthetic approaches focused on the preparation of new cage topologies whose structural, constitutional and electronic characteristics can give rise to attributes with potential applications in **catalysis**,[1-4] **drug delivery**,[5] **sensing**[6,7] and others.[8] Most commonly applied synthetic approaches to functional capsular entities use the formation of kinetically stable binding geometries or coordination complexes with defined ligand-accessible sites and which direct the assembly into capsular entities. Amongst the most remarkable cage systems, are examples that exemplify **enzyme-type reaction characteristics**,[9,10] whereby confined host-guest environments influence the transition states and catalytic performances.

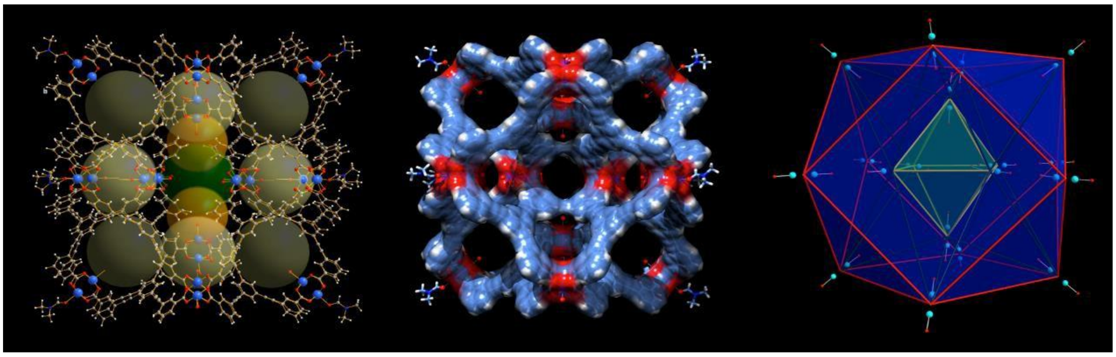

Figure: Structure and topological representations of a coordination cage with exceptional cross-sectional diameters consisting of 36 Cu(II) ions and 24 organic ligands The cage structure is composed of multiple sub-cages providing numerous distinctive binding sites through labile coordination solvent molecules (see. Schmitt et. al. *Nature Communications,* **2017**, DOI:10.1038/ncomms15268).

The Senior Sophister project will be assisted by a postgraduate/postdoctoral researcher and may involve the following key aspects:

a) **Synthesis of new coordination cages involving a combination of organic and inorganic synthetic approaches.** The ligands will be synthesised *via* multi-step organic synthesis and characterised by NMR and IR spectroscopy.
b) **Structural analyses of the coordination compounds using single crystal X-ray diffraction**. Further characterisations may focus on the spectroscopic properties, thermal stability, etc.
c) **Instigation of guest-host chemistry**, e.g. investigation of the incorporation and release of drug molecules (drug delivery), catalysts or photo-active molecules.
d) **Evaluation of properties of the cages/coordination compounds**, e.g. in the areas of bio-inspired oxidation catalysis/enzyme mimetics, or drug-delivery, cell uptake or sensing.

References: **1** M. Yoshizawa, M., J. K. Klosterman, M. Fujita,. *Angew. Chem. Int.Ed.* 2009, **48**, 3418; **2** M. D., Pluth, R. G. Bergman, and K. N. Raymond, *Acc. Chem. Res.* 2009, **42**, 1650; **3** S. Leininger, B. Olenyuk and P. J. Stang,. *Chem. Rev.*2000, **100**, 853; **4** Q.-Q. Wang, S. Gonell, S. H. A. M. Leenders, M. Dürr, I. Ivanović-Burmazović and J. N. H. Reek, *Nat. Chem.* 2016, **8**, 225; **5** B. Therrien, *Top. Curr. Chem.* 2012, **319**, 35.; **6** J. Wang, C. He, P. Wu, J. Wang and C. Duan, *J. Am. Chem. Soc.* 2011,.**133**, 12402; **7** X. Yan, T. R. Cook, P. Wang, F. Huang and P. J. Stang, *Nat. Chem.* 2015, **7**, 342.; **8** M. D. Ward and P. R. Raithby, *Chem. Soc. Rev*. 2013, **42**, 1619; **9** C. J. Hastings, D. Fiedler, R. G. Bergman and K. N. Raymond, *J. Am. Chem. Soc.* 2008, **130**, 10977; **10** M. J. Wiester, P. A. Ulmann and C. A. Mirkin, *Angew. Chem. Int. Ed.* 2011, **50**, 114.

Towards H_2 Economies: 4th Generation Metal-Organic Frameworks for Photo/Electro-Catalytic Device Fabrication

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Scientific objectives: The project addresses the question of how catalytically active Metal-Organic Frameworks (MOFs) or light-harvesting MOFs can be synthesised deposited or printed on electrodes to produce electro/photo-catalytic devices. The systems will be used to catalyse highly endergonic, energy-related chemical transformations (e.g. H_2O oxidation, & CO_2 reduction, H_2 formation). The performance of the devices incl. catalytic activity, stability and efficiency will be investigated.

Scientific background: MOFs are regarded as key compounds related to energy storage and conversion, as their unprecedented surface areas make them promising materials for gas storage and catalysis.[1] We believe MOFs allow the replication of key features of natural enzymes thus demonstrating how size, shape, charge and functional group availability greatly influences the guest binding and performances in catalytic reactions.[2] [3] In view of sustainable energy-related applications, the research project is directed towards electro/photo-catalytic systems. Photosynthesis is the process by which plants, algae and some bacteria use light energy to split water and use the released electrons and protons for the reduction of CO_2 to produce sugars. The process stores energy in chemical bonds. Insights into molecular details of these conversions can guide us towards employing renewable energy sources to produce fuels in highly porous MOFs whereby the term 'fuel' in a broader sense can be thought of as a reduced molecule that can efficiently be oxidised to produce desired compounds or energy as required.

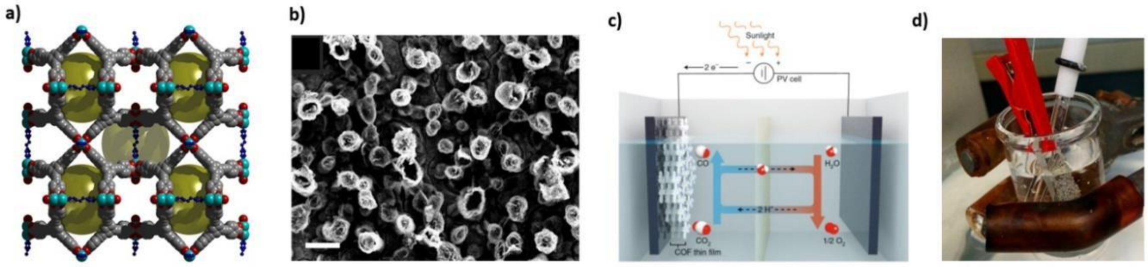

Figure: a) Crystal structure of catalytically active MOF; b) MOF grown on ITO electrode (SEM micrograph); c) Electrochemical cell setup; d) Catalytic water oxidation using MOF/ITO electrode.

The project will involve on the following defined parts:

- **Synthesis of MOFs:** This task will involve the preparation, structural and physicochemical characterisation of MOFs using novel, catalytically active clusters and organic linkers. The applied methodologies are well established with the research group.
- **Deposition of MOFs on electrodes:** The heterogeneous MOF materials will be interfaced or electrochemically deposed a t
- he electrode materials.
- **Characterisation of the electrodes:** Characterisation techniques will involve electron microscopy techniques, X-ray diffraction and spectroscopic methods (Raman spectroscopy & XPS).
- **Electro-catalytic reactivity studies:** The electrodes will be applied to catalyse highly endergonic, energy-related oxidation or reduction reactions (e.g. H_2O oxidation, H_2 production or CO_2 reduction). The performances and the stabilities of the electrodes will be optimised.

References: [1] Furukawa et al., *Science* **2013**, *341*, 1230444; [2] Diercks et. al. *Nature Materials* **2018**, *17*, 301. [3] Schmitt et al. *Nature Communications*, **2017**, DOI:10. 1038/ncomms15268.

Organic, Medicinal and Biological Chemistry

Anhydrides as Nucleophiles!

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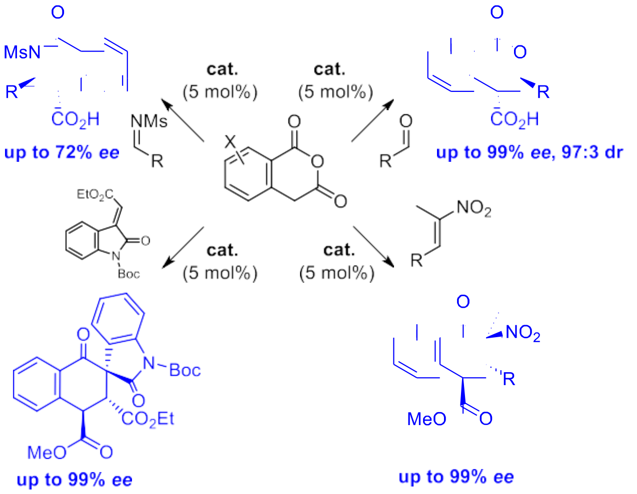
Anhydrides have been used as electrophilic acyl transfer agents for over a century and their chemistry is almost completely dominated by their electrophilicity. We have recently developed a completely new catalytic asymmetric class of reactions in which an anhydride can act as a nucleophile and react with a range of electrophiles to give products of enormous medicinal interest with excellent stereocontrol.

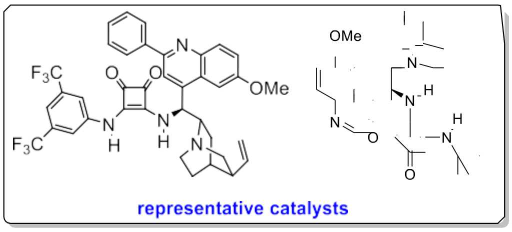
We wish to fully exploit this technology along multiple lines – principally by expanding the substrate scope to include different anhydrides, but also through and innovative catalyst design

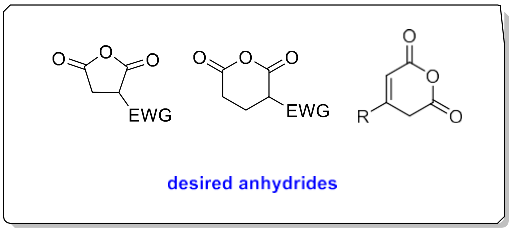
Would particularly suit a student who:

a) Can work out a plausible mechanism without reading the references below (**hint**: look carefully at the anhydride structures - the catalyst can act as a weak acid and a weak base simultaneously).

b) Would be interested in working on a real, current problem. A challenging but potentially rewarding project.







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School of Chemistry Senior Sophister Research Project 2021

A new approach to asymmetric nucleophilic catalysis

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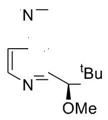
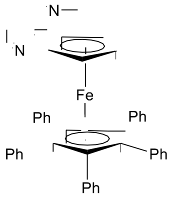
N,N-dimethylaminopyridine (DMAP) is the quintessential nucleophilic catalyst. In order to use the catalyst in asymmetric transformations one needs to install chirality. This poses a problem: in order to control the stereochemical outcome of a reaction it is best to install the stereochemical information as close to the nucleophilic nitrogen atom as possible; however, any steric bulk here significantly retards the nucleophilicity of the catalyst and destroys activity. Several designs have been reported (including from our group – see below) which attempt to extend the influence of remote chirality over the endocyclic nitrogen atom, without hampering nucleophilicity to a significant extent – with limited success. There thus exists an activity-selectivity conundrum associated with all such systems, which seriously hampers the field.



Vedejs

J. Am. Chem. Soc. **1996**, *118*, 1809



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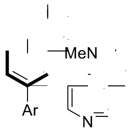
Acc. Chem. Res. **2000**, *33*, 412



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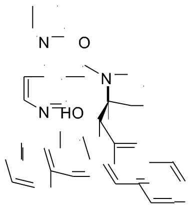
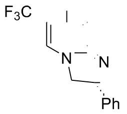


Connon

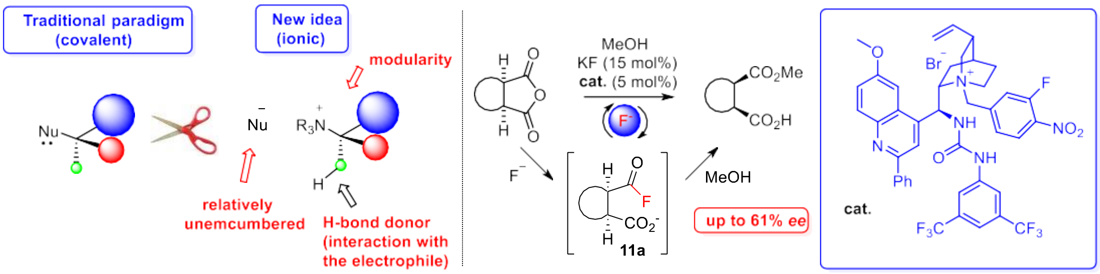
Org. Biomol. Chem. **2005**, *3*, 981
Org. Biomol. Chem. **2006**, *4*, 2785



Birman

J. Am. Chem. Soc. **2004**, *126*, 12226

Recently, we have taken an entirely different approach: the divorce of the nucleophilic and chiral units completely through the design of chiral ionic catalysts. These are devised so that the nucleophilic anion can be as small as possible, and the chiral cation as large as possible, with the proviso that it must have functionality allowing it to interact with the electrophilic reaction component. This completely new approach allows the practitioner to 'have their cake and eat it': fast but also selective catalysis. We reported the first such example last year.



Chem. Commun. **2018**, *54*, 10108

In this project we intend to both refine the catalyst design and apply it in a range of transformations in which traditional catalyst systems are inadequate.

School of Chemistry Senior Sophister Research Project 2021

Exploitation and prebiotic significance of ancient biomolecules

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(with collaboration with Prof Mike Southern)
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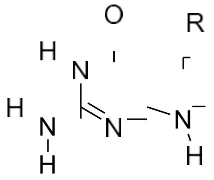
Research Project Description:

Deazapurines are an intriguing class of molecules, they are extremely rare in biological systems yet, in each of the 3 domains of life (archaea, eubacteria and eukaryotes), a slightly different, but related, deazapurine (DAP) is a substrate for an ancient enzyme. In each of the 3 domains a similar enzyme performs a similar task - it exchanges the appropriate DAP for a specific guanine in the transfer RNA (tRNA) of that organism. In bacteria and eukaryotes the appropriate DAP is exchanged with a guanine at position 34 (the wobble position of the anti-codon) but in archaea the DAP is exchanged with a guanine at position 15. Given that these 3 DAPs and enzymes alter the machinery of protein synthesis, are ancient and ubiquitous it is extremely surprising that their role within any of the 3 domains of life is poorly understood. In the case of eukaryotes, it is thought that the ancient enzyme was present in the last common eukaryotic ancestor and predates mitochondrial incorporation.

We have recently shown that analogues of these compounds can have a dramatic effect on eukaryotic systems and we are keen to build upon these results. There are **4 projects available** that will focus on the preparation of new analogues targeted at the different domains of life. Furthermore, a link to the prebiotic world is envisaged and a speculative investigation into this area could be undertaken.

	
General structure of deazapurines	Transfer RNA

Initial work in this area has led to the design of a novel nucleobase that exhibits unprecedented therapeutic efficacy in a mouse model of multiple sclerosis.

References:

S.J. Connon and J.M. Southern, Substituted Pyrimidine Derivatives useful in the Treatment of Autoimmune Diseases, WO2016050804 A1; S. Varghese, M. Cotter, F. Chevot, C. Fergus, C. Cunningham, K.H. Mills, S.J. Connon, J.M. Southern, and V.P. Kelly, *Nucleic Acids Res*., 2017, **45**, 2029 – DOI: https://doi.org/10.1093/nar/gkw847

Synthesis of luminescent supramolecular polymers and hydrogels

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gunnlaut@tcd.ie

Research Project Description:

The objective of this project is to develop and synthesize simple organic ligands that upon coordination to lanthanide ions such as Eu(III) and Tb(III) can give rise to the formation of novel luminescent supramolecular polymers and hydrogels. Recently, there has been great interest in the field of supramolecular- and material chemistry, as well as in nanotechnology in the development of functional transparent gels and supramolecular polymers, formed by using week non-covalent interactions such as hydrogen bonding, pi-pi stacking and electrostatic interactions.[1,2] In contrast, the use of metal-directed gelation in developing such supramolecular structures has only recently been explored,[3] but their use enable the formation of more ordered structures, in multiple directions (*i.e.* 2D and 3D) with added complexity and function. We have recently undertaken the development of several organic ligands that can be used in such metal directed synthesis of (hydro) gels and polymers, all of which are either colorimetric or luminescent. One of our samples is shown in Figure 1a. Here we used simple three arm ligands based on the use of C_3-symmetrical benzene-1,3,5-tricarboxamide (**BTA**), and through a covalent spacer, tethered three 2,2′6′,2′′-terpyridyl (*tpy*) moieties to this central core. Then by using lanthanide ions, the formation of highly ordered gels has been achieved, as is demonstrated in Figure 1b, using Scanning Electron Microscopy.[4] The aim of this project is to further develop this idea by changing the nature of **a)** the spacer used in connecting **BTA** to the *tpy* by using chiral building blocks and **b)** by changing the *tpy* ligands for other metal coordinating ligands to allow for the use of verities of other metal ions. We will then, **c)** investigate their spectroscopic properties in solution and in the solid state, and **d)** investigate the morphology of the gels formed from these ligands using various imaging techniques in collaboration with Prof. John Boland, as well as we will investigate the rheology of the material formed.

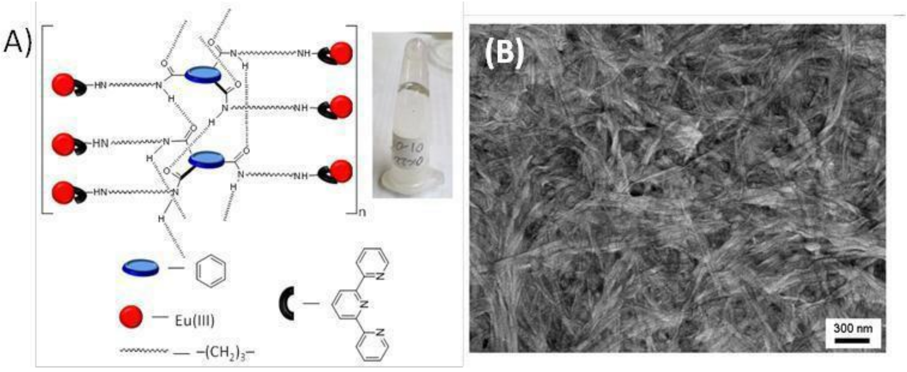

Figure 1. A) Terpyridine-based tripodal ligand (**L**) showing the europium binding sites that give rise to the formation of **$EuCl_3$-L**. B) SEM images of **$EuCl_3$-L**.

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Naphthalimide based Tröger's bases as DNA targeting molecules

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Research Project Description:

The aim of this project is to develop DNA targeting/binding luminescent probes and novel therapeutics for targeting cancer cells and will be carried out in collaboration with Professor John M. Kelly. The general structure of the target molecules are shown in Figure 1a and are based on the use of 1,8-naphthalimide chormophores, which can be synthetically modified at the imine side as well as on the aromatic unit itself. The Tröger's base is a well-known chiral cleft-shaped molecule, containing a diazocine ring, conjugated to two aromatic moieties. The chirality, with a C_2 axis of symmetry, is provided by the presence of the two bridgehead sterogenic nitrogen atoms of the diazocine ring.[1] We have recently employed this structure in the development of DNA targeting compunds[2], and for use as luminescent cellular imaging agents, as demonstrated in Figure 1b[3]. The main objectives of this SS project are to: **a)** Synthesize two new naphthalimide based Tröger's bases, based on the use of polyamines at the imide terminus. This is achieved in 3-4 steps synthesis depending on the nature and the length of the polyamines. If time allowed, the enantiomers will be separated using a column chromatography procedure developed in the laboratory of Professor Kelly. **b)** We will then investigate the binding of these to DNA by using absorption and fluorescence titrations and the binding strength and mode analyzed further by using thermal melding experiments, as well as CD and LD spectroscopies. **c)** Finally the biological properties of these compounds will be probed in collaboration with Prof. Clive Williams in the School of Biochemistry and Immunology.

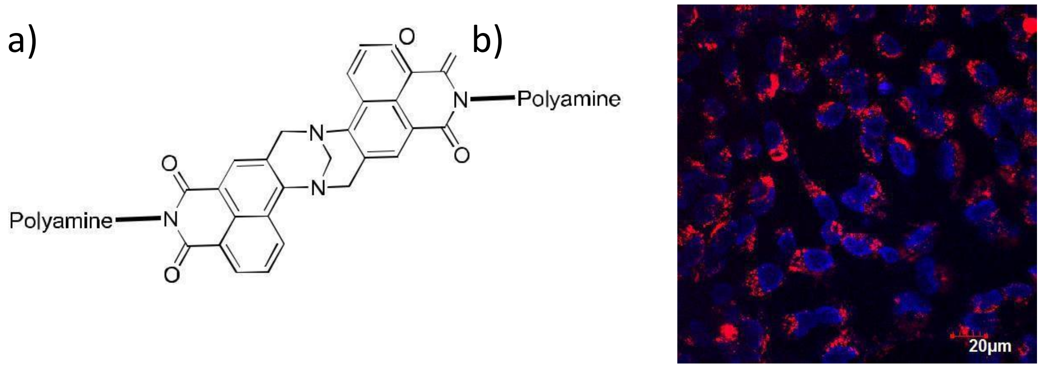

Figure 1. a) General structure of the Tröger's bases developed in this project. b) The confocal fluorescence image of a Tröger's base within HL-60 cells.

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Self-Assembly of Tröger’s Base Based 2D Metallacycles

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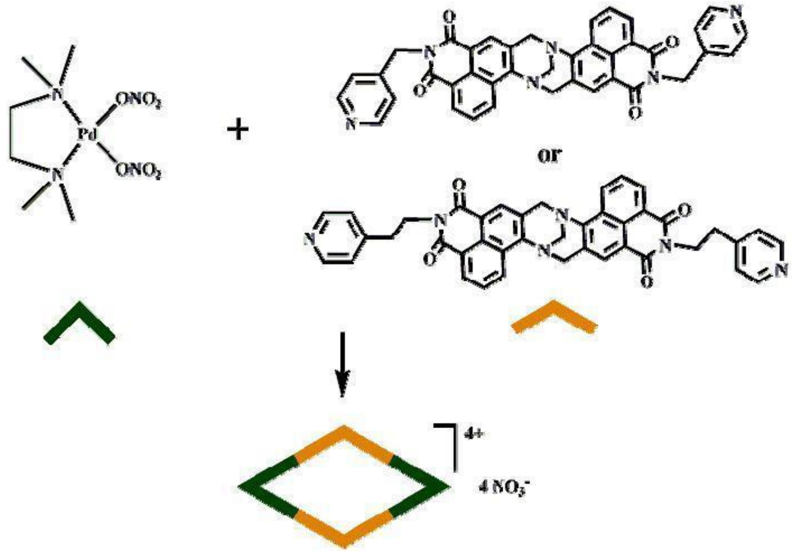
Research Project Description:

The underlying aim is to design and synthesis of novel shape- selective building blocks based on Trögers-base motif and they will react with *cis*-blocked Pd(II)/Pt(II) acceptors to make several [2+2] self-assembled chiral, fluorescence metallamacrocycles, that can be employed in gas-storage, chemosensing, DNA Binding and live cell-imaging. Examples of the kind of ligands that will be developed in this project are shown below. Incorporation of 1,8-naphthaliimide fluorophore causes the final macrocycles to exhibit strong emission characteristics. Having large internal concave aromatic surface, the final macrocycles (shown schematically belwo) are expected to act as macrocyclic receptor for large spherical convex guest such as C_{60}/C_{70}. The host-guest binding will be demonstrated using various spectroscopic methods (UV, Fluorescence, ^{13}C NMR and ESI- MS).



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Synthesis of novel ligands for lanthanide ions using ‘click’ chemistry

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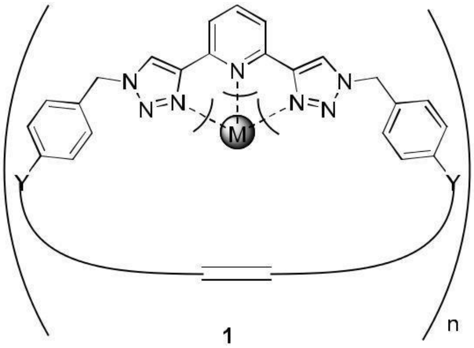
Research Project Description:
The objective of this project is to develop several new ligands based on the pyridyl unit shown below for use as novel coordination ligands for lanthanide and transition metal ions. These will be made by employing copper catalyst 1,3-dipolar cycloaddition (1,3-Huisgen) reaction reactions using variety of appropriate functionalised azides and alkyl derived pre-cursers. The use of ‘click’ chemistry to develop novel and functional organic structures form simple or complex molecules has become highly popular in recent times.[1] There use for developing novel ligands for metal coordination has, however, only recently been explored. We have developed various lanthanide luminescent systems, where two macrocyclic cyclen based complexes were conjugated together by the use 1,3-Huisgen reaction.[3] Recently we have extended this area of research further towards the development of structures such as **1** shown below, that are formed in a few steps synthesis from 2,6-bis((trimethylsilyl)ethynyl)pyridine. Compound **1** is currently being developed in our laboratory as a part of a PhD project. This system is formed by firstly using the ‘click’ chemistry to give an acyclic pyridyl di-triazole ligand which upon reaction with lanthanide ions such as Eu(III) can form a 1:3 (metal:ligand) complex, while using Ru(II) gives the 1:2 complex formation. These ions preorganise the ligand to allow for macrocyclisation reaction to take place; which can be achieved by using Grubbs’ catalysed olefin ring-closing metastasis reaction. This gives interlocking supramolecular architectures such as [n]catenane and [n]rotaxane. The objective of this SS project is to build on this work and to develop two to three new ligands based on **2**, where both the pyridine as well as the phenyl ring will be synthetically modified in positions *X* and *Y* respectively. The aim is then to use the above ions (and possibly several others) to template the synthesis of novel supramolecular structures from these new ligands. The underlying aim is to form new luminescent material that can be employed for instant in cellular imaging and in luminescent sensing. Consequently, in-depth spectroscopic analysis uing both UV-Vis absorption and luminescence of **2** with these ions will be undertaken.



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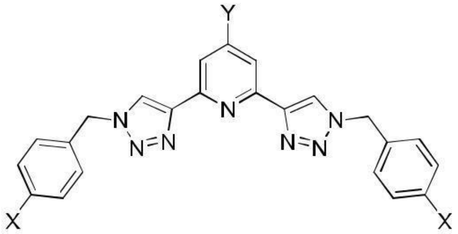

2

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School of Chemistry Senior Sophister Research Project 2021

β-Hairpin Cyclic Peptides as Inhibitors of Nucleotide Excision Repair

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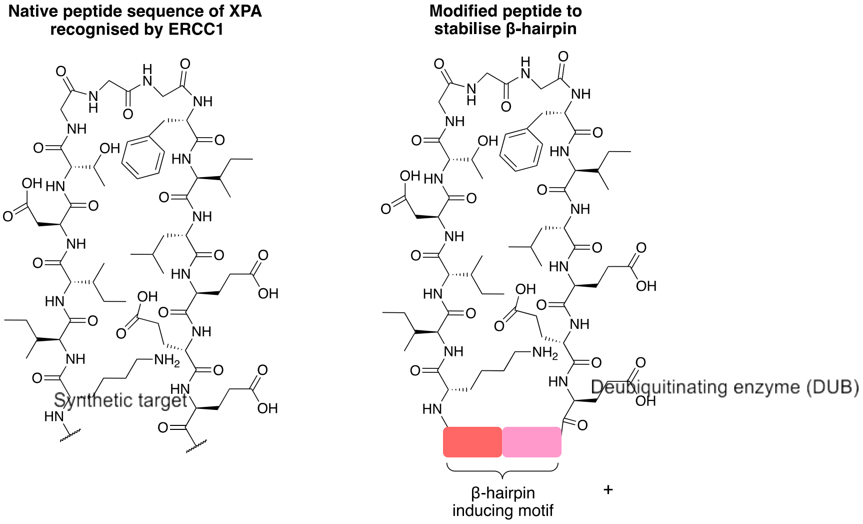
jmcgoura@tcd.ie

Targeting the DNA repair response is one of the most compelling and, as yet poorly exploited strategies for sensitising or re-sensitising tumours to DNA alkylating chemotherapy. Nucleotide excision repair (NER) is a key DNA damage repair pathway.[1] However many NER proteins are structurally disordered and, as such, hard to target for therapeutic intervention.[2] A key protein-protein interaction (PPI) in the NER pathway occurs between XPA protein and the endonuclease XPF-ERCC1.[3] Blocking the XPA-ERCC1 interaction thus prevents NER, and so can re-sensitize tumors to chemotherapy.[4]

Targeting protein-protein interactions (PPIs) expands what we can consider druggable targets beyond simple enzymes and receptors. However due to the large PPI surface small molecule inhibitors can lack efficacy. Cyclic peptides can confer increased specificity, particularly when targeting PPIs. β-hairpins are found at the active sites of variety of PPIs, making them ideal candidates for drug leads. Typically, these molecules are replicated synthetically and cyclised *via* the use of a β-turn template that can be derived from almost any β-turn-inducing motif.[5]

This aim of this project is to synthesize, characterize and test cyclic hairpin shaped peptides to mimic the binding motif of XPA. The student will gain experience in solid phase peptide synthesis, peptide purification (HPLC) and a variety of characterization techniques.



Native peptide sequence of XPA recognised by ERCC1

Modified peptide to stabilise β-hairpin

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School of Chemistry Senior Sophister Research Project 2021

Synthesis of photoactivatable inhibitor of a DNA damage repair enzyme

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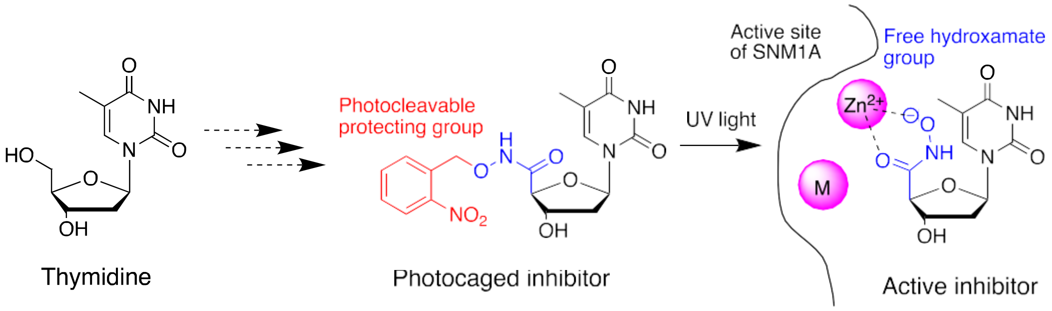
Research Project Description:

DNA damage repair enzymes play crucial roles in cell maintenance. SNM1A is a key DNA damage repair enzyme acting as a 5’-3’ exonuclease, about which little is known. It plays vital roles in DNA repair, immune system development and telomere maintenance and has been linked to chemotherapy resistance.[1, 2] Despite its clear biological importance in cancer therapy, immunity and ageing, few inhibitors of this enzyme have been reported.

A nucleoside-based inhibitor of SNM1A has been reported by the McGouran group.[3] This inhibitor was synthesised *via* the incorporation of a hydroxamic acid group on the 5’-position of thymidine. The aim of this project is to generate a photoactivated derivative of this lead inhibitor for potential use in photochemotherapy. This will involve the installation of a photocleavable protecting group on the 5’-hydroxamic acid group.

The photocaged inhibitor will be generated by chemical synthesis of the 5’-modified nucleoside, using methodologies recently developed in the laboratory. Biological evaluation and photocleavage studies of the inhibitor will be carried out as time allows. The student will gain valuable skills in organic synthesis as well as biochemical and biological techniques.



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School of Chemistry Senior Sophister Research Project 2021

Molybdenum-Based Catalysts for Allylic Trifluoromethylation

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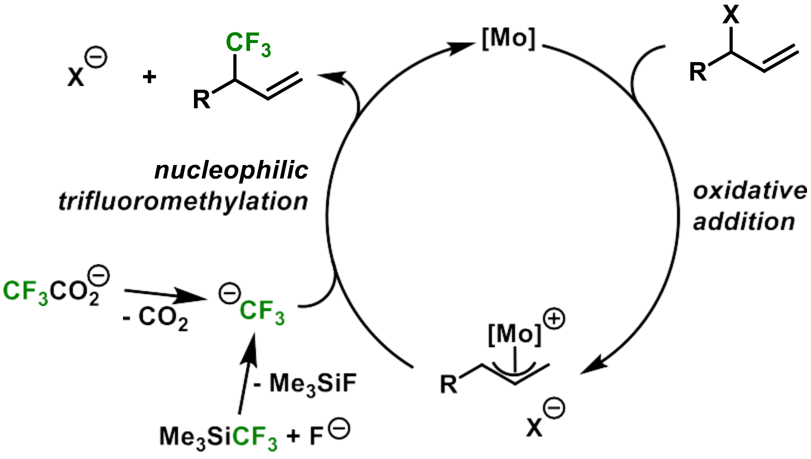
Research Project Description:

The incorporation of fluorine into organic compounds is of enormous significance in medicinal chemistry: as a small and highly electronegative atom, its presence can have profound effects on the chemical and biological properties of a molecule.[1] However, the extreme difference in reactivity between fluorine and the other halogens means that methods developed for the formation of C-Cl/Br/I bonds cannot be easily translated to C-F bond formation. The incorporation of CF_3 groups is particularly important, and is often reliant on expensive and highly reactive reagents – general methods are still lacking.

This project will explore the potential for Mo^0 complexes to catalyse the trifluoromethylation of allylic electrophiles (see proposed catalytic cycle below). Mo-based catalysts generally give branched products in allylic alkylation reactions, in contrast to Pd or Cu.[2] Previous work in the lab has demonstrated that nucleophilic attack by CF_3^- liberated by trifluoroacetate decarboxylation is possible, but that decarboxylation is very slow at 130 °C.[3] This project will continue to explore this pathway, as well as the use of more convenient (though costlier) sources of CF_3^- such as the Ruppert-Prakash reagent, Me_3SiCF_3, which should allow for lower reaction temperatures and higher-yielding reactions.



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School of Chemistry Senior Sophister Research Project 2021

Studies into the Mechanism of Allylic Trifluoroacetate Rearrangements

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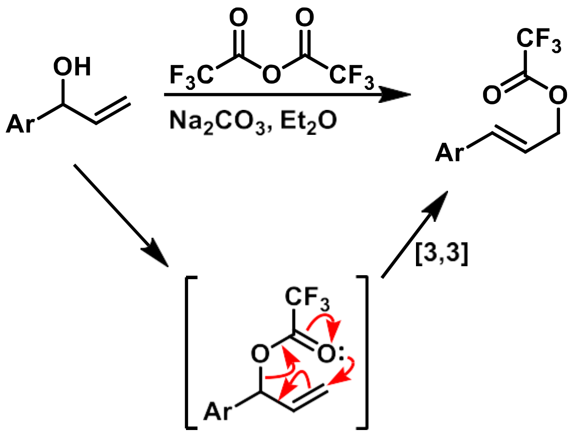
Research Project Description:

While preparing substrates for a different project (CP1 – see above), we observed an unexpected rearrangement reaction when acylating branched allylic alcohols – instead of obtaining the expected branched products, we occasionally found that the linear product formed preferentially.[1]



pseudopericyclic [3,3]?

There are a number of potential mechanisms by which this could occur, the most likely would seem to be the pseudopericyclic [3,3]-sigmatropic rearrangement shown above.[2] Similar mechanisms have been implicated in related systems.[3]

The aim of this project is to develop a better understanding of the scope and mechanism of this process. This will involve some organic synthesis, and then physical organic chemistry studies. This is likely to focus on establishing linear free-energy relationships (e.g. Hammett plots) and measuring reaction kinetics, but could potentially include the measurement of kinetic isotope effects, or computational chemistry (DFT), if this aligned with the students' interests.[4]

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School of Chemistry Senior Sophister Research Project 2021

Guanidine piperazines to fight *Mycobacterium* infections

Prof. Isabel Rozas (IR1)
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Research Project Description: Regardless of the good progress in modern therapies to fight tuberculosis, the pathogen responsible of this disease, *Mycobacterium tuberculosis* (Mtb), is far from being eradicated. Resistance, persistence and co-infection with HIV make difficult the complete cure of this infection with current treatments. Hence, there is an urgent need to develop new drugs to treat mycobacterial infections.[1] Recently, the evaluation of a small library of amidine piperazine analogues (Fig. 1) in an *in vitro* assay against a Mtb strain has been reported,[2] and some of these compounds showed high antitubercular potency.

Even though a clear target was not established, the good antibacterial results reported as well as the known amidine-guanidine similarity, encouraged us to screen a number of guanidine derivatives from our in-house compounds' library[3] in collaboration with Prof. Stephen Gordon (Conway Institute-UCD). Because of the safety problems associated to the causative agent of tuberculosis (Mtb) due to its slow growth and high virulence, these compounds have been tested against *BCG* which is prepared from an attenuated strain of bovine tuberculosis bacillus, *Mycobacterium bovis*, that has lost its ability to cause disease in humans. So far, results have shown that some of these guanidine analogues (Fig, 2 green) are quite active against BCG.

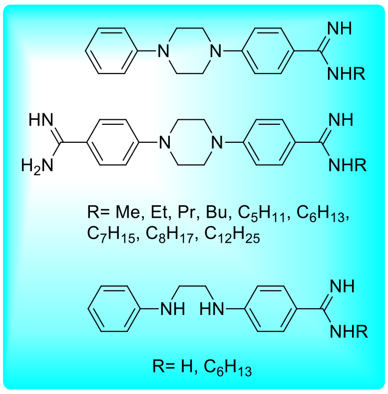

Figure 1

Thus, in a ligand-based design approach, in this project we will prepare new piperidine/ piperazine guanidines (Fig. 2, purple) and, we will test their anti-mycobacterial activity, in collaboration with Gordon's lab, using a resazurin microtitre plate method.[4] Minimum inhibitory concentrations (MIC) for the tested compounds will be calculated, with the antibiotic kanamycin used as a positive control. Moreover, a study of the physicochemical properties of the compounds (logP, logD, pK_a) will be carried out to find correlation to their potential activity.

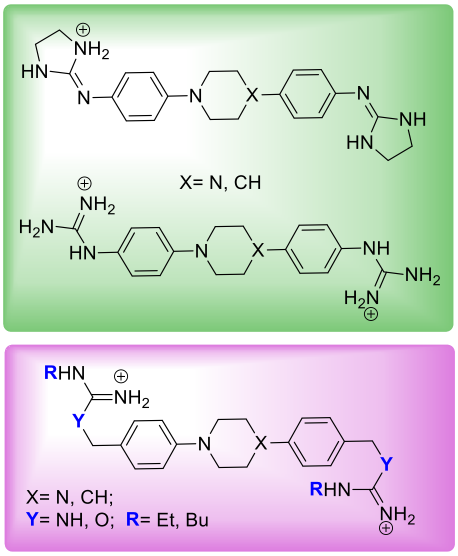

Figure 2

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School of Chemistry Senior Sophister Research Project 2021

Targeting Guanine-Quadruplexes in a dual attack

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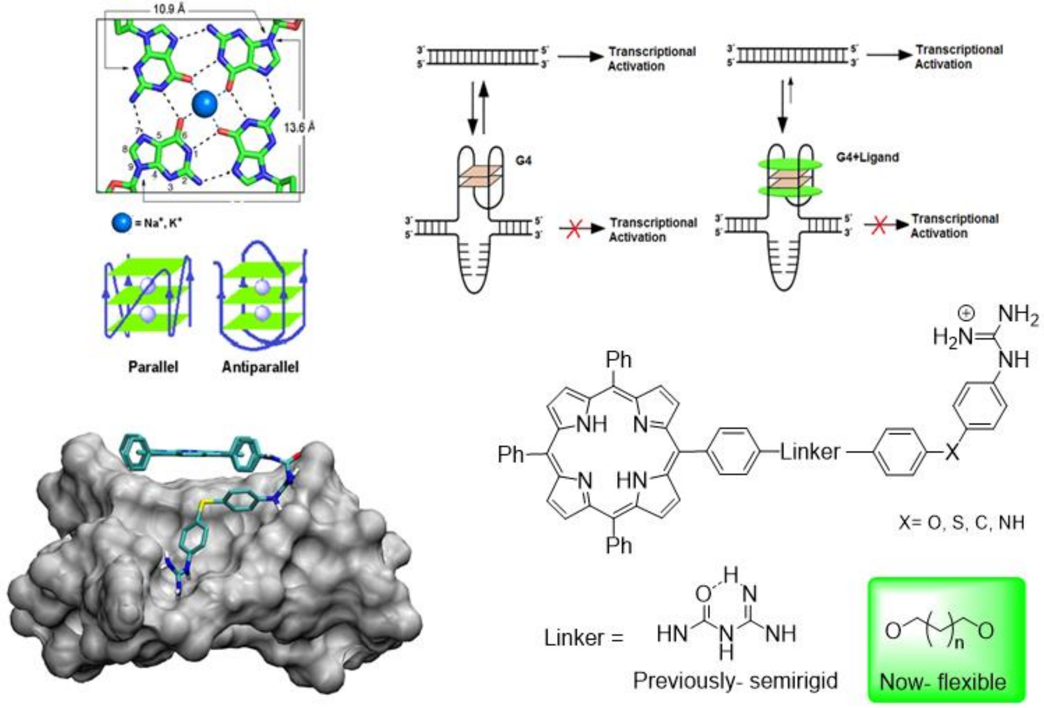
Research Project Description: Nucleic acids within the cell are not only present as the classic Watson-Crick duplex, but also can form different non-canonical, multi-stranded structures such as guanine quadruplexes (G4s). These G4s are 3D structural arrangements formed by G-rich DNA regions resulting from the stacking of several *G-quartets* stabilized by cations such as Na^+ and K^+ (Fig. upper left).[1] G4s are stable under physiological conditions and have been visualized *in vivo* in human cells.[2] Also, they are involved in numerous diseases such as HIV, malaria, Alzheimer's, ALS or cancer. G4s are present in biologically important regions, such as the telomeres end (h-Tel) as well as in the regulatory regions of oncogenes (*e.g.* c-MYC, c-KIT, B-Raf, K-Ras).[3] Formation of G4s in gene promoters results in the suppression of transcription; therefore, ligands that stabilized G4s in those promoters will inhibit transcriptional activation (Fig. upper right).

We have recently developed a series of porphyrin-diaromatic guanidine conjugates connected by a semirigid linker that selectively bind to G4s over dsDNA (Fig. down).[4] Thus, based on our previous results and modelling the objectives of this project are i) to synthesize fluorescent and selective G4 probes by conjugating diaromatic guanidines with appropriate porphyrins by means of flexible linkers (Fig. down right), and ii) the biophysical study of the binding and selectivity of the prepared ligands to different G4s and dsDNA by means of biophysical techniques (i.e. UV-thermal denaturation, CD).



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Development of a Peptide Macrocyclization Strategy Towards Synthesis of Ovarian Cancer Therapeutics

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In the last decade over 30 peptide based drugs were approved for clinical use in the EU. This represents approximately 3% of all drugs approved in the EU in the last decade and it is believed that the focus will continue to shift onto peptide based therapeutics in the coming years as new diseases emerge and still incurable ones persist. With this comes a need for more practical and efficient strategies to access peptide structures synthetically. Cyclic peptides in particular have increased resistance to peptidases compared to their linear counterparts due to the absence of either terminus giving them potentially greater bioavailability and making them very attractive drug candidates.[1, 2] This research project will specifically focus on the development of a cyclization methodology for synthesizing cyclic peptide structures.

Groundbreaking techniques in peptide synthesis such as solid-phase peptide synthesis (SPPS)[3] and native chemical ligation (NCL)[4] have allowed the number, size and variety of synthetically accessible peptide structures to explode. However these techniques are not without their limitations. Cyclization of a linear peptide using NCL is limited to those containing a cysteine or alanine residue. This project aims to use the thiol-ene 'click' reaction to insert a thiol group into alternative amino acids thus expanding the scope of residues that can be used at an NCL site for cyclization. The cyclic DWLPK peptide, which has been shown to be effective in treating mice with patient-derived xenografts of metastatic ovarian cancer,[5] is a model target for demonstrating this methodology due to the lack of either a cysteine or alanine in its structure.

Over the course of this project the student will become familiar with valuable synthesis and analytical techniques such as SPPS, NCL, non-natural amino acid synthesis, NMR, mass spectrometry and HPLC. This project is aimed at students that are interested in using synthetic organic chemistry for wider biological applications.

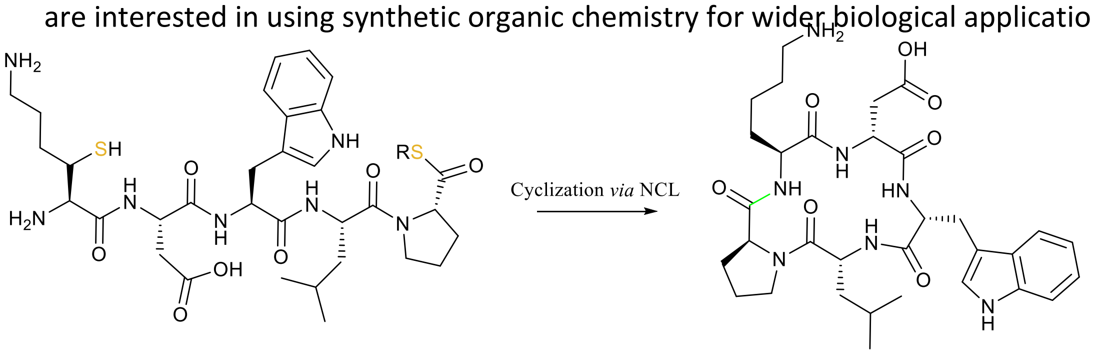

Figure 1. Cyclization of linear peptide precursor to synthesize the cyclic DWLPK peptide

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Synthesis of a potential SARS-CoV-2 peptide therapeutic using a novel aspartic acid mediated peptide ligation

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Research Project Description:

Peptide drugs have revolutionised modern medicine and continue to be a major focus of pharmaceutical R&D. The chemical synthesis of large peptides as a single chain is impractical due to incomplete reactions, difficulties with purification and low overall yields. Recombinant methods for peptide synthesis also suffer from the formation of heterogenous mixtures. Modern strategies for peptide synthesis involve the ligation of two smaller peptide fragments which can be reliably synthesised using Solid Phase Peptide Synthesis (SPPS). The Native Chemical Ligation (NCL) methodology developed by Kent *et al*. in 1994 has revolutionised chemical peptide synthesis.[1] However, its use is restricted by the requirement for the relatively rare amino acid cysteine at the ligation site.

The aim of this project is to develop a ligation methodology that overcomes the need for cysteine. The approach will involve the incorporation of an unnatural thioaspartic acid residue at the ligation site to mediate the ligation reaction. After ligation, the thioaspartic acid may be converted into the relatively common amino acids, aspartic acid or alanine, under mild, metal-free and green conditions.

This novel ligation methodology will be demonstrated through the synthesis of the promising SARS-CoV-2 peptide therapeutic, LCB1, designed by Cao *et al*.[2] LCB1 is a 56-amino acid peptide that binds to the spike protein of SARS-CoV-2 and inhibits viral attachment with IC_{50} values in the picomolar range (**Fig. 1**). The student undertaking this project will gain experience in the organic synthesis of unnatural amino acids, Solid Phase Peptide Synthesis (SPPS) and peptide purification (HPLC). The project would appeal to students interested in medicinal chemistry, organic synthesis and drug discovery.

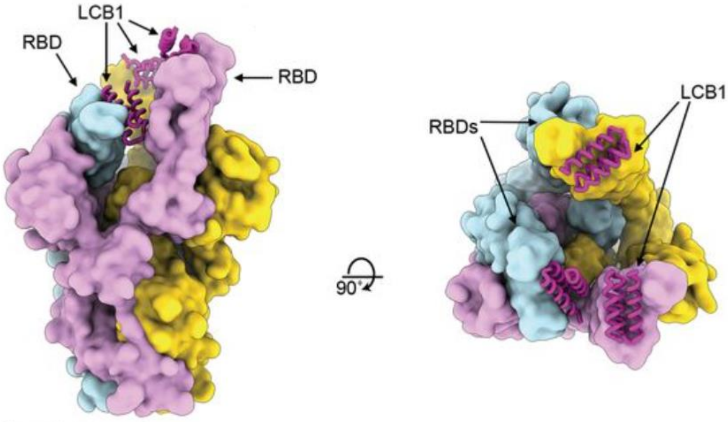

Figure 1. LCB1 bound to the receptor binding domains (RBDs) of the spike protein of SARS-CoV-2.[2]

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The Pigments of Life – Chemistry of Tetrapyrroles

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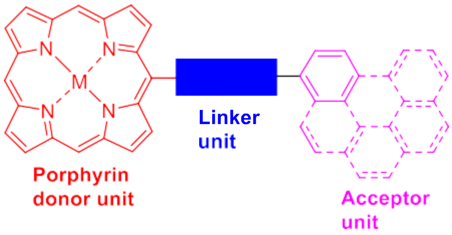
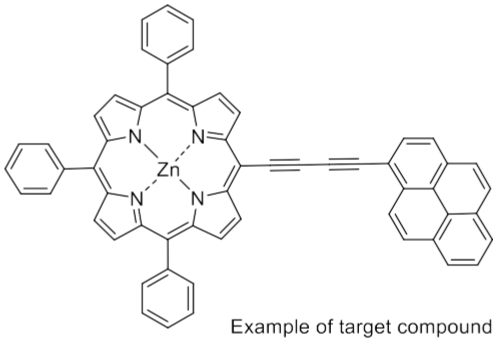
Research Project Description:
Tetrapyrroles are a unique class of ubiquitous natural compounds and are targets of strategic importance in biology, industry (pigments, catalysts, sensors, nanomaterials) and medicine (cancer therapy and neuropsychiatry). Recent breakthroughs in their synthesis, biochemistry, industrial use, and medicinal relevance are opening tremendous application opportunities in bio- and information technology. We use tetrapyrroles as biologically relevant 'molecular systems' for an interdisciplinary approach towards health and materials science research.
Currently our chemical studies focus on the unique optical, photophysical, biological, and structural properties of porphyrins. In order to fully utilize the application potential of tetrapyrroles we aim:

- to overcome existing limitations in the synthetic accessibility of porphyrins,
- to advance the understanding of the interrelationship between their chemical properties and biological function, esp. with regard to energy and electron transfer processes.
- to construct porphyrin-based nanomaterials on surfaces as intelligent electrooptical materials.

Donor-acceptor chromophore arrays play a crucial role as light harvesting systems in nature. To study the role of spatial orientation and distance for the electronic and energetic communication between such donor-acceptor moieties, our group investigates in the synthesis of chromophore dyads that are connected by different spacer as well as rigid linker groups.





Example of target compound

Objectives:

- Synthesis and characterization of porphyrins-perylene/pyrene dyads.

Tasks:

- Synthesis of porphyrin precursors via condensation reactions.
- Introduction of functional groups suitable for organometallic coupling reactions.
- Optimization of Suzuki, Sonogashira and click reactions for coupling with aromatic acceptor units.
- Photophysical characterization of donor-acceptor dyads.

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Core-accessible Free Base Porphyrin Receptors

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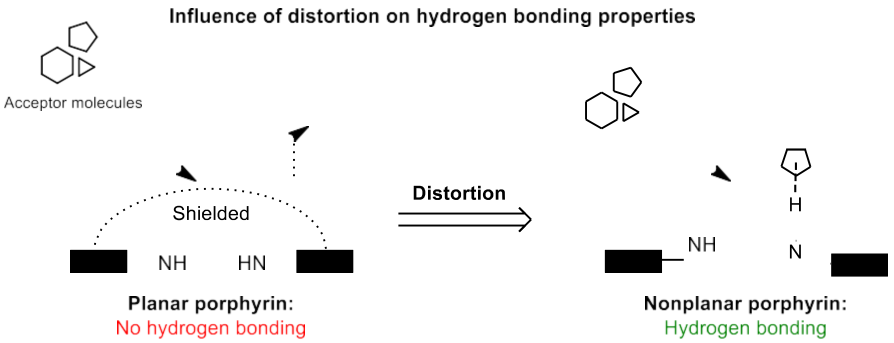
Research Project Description:

Porphyrins are involved in all aspects of life, materials science and medicine and play an important role as cofactors, regulators, drug targets, clinical agents and (photo)active reagents. Much of their chemical reactivity relates to specific macrocycle conformations, i.e. the inherent flexibility of the tetrapyrrole macrocycle which can be modulated by metal, steric and environmental effects. Thus, porphyrins can exhibit different distortions of the aromatic system ranging from planar to highly nonplanar. Typically, porphyrin-metal complexes are used in nature for countless biocatalytic processes. Their catalytic activity is dependent on a metal ion complexed by the tetrapyrrole scaffold and they offer an economic and efficient method to accomplish a wide range of fundamental organic transformations.

A new concept, porphyrin-based organocatalysis and sensing utilizes nonplanar free base tetrapyrroles for the activation and binding of small molecules *via* hydrogen bonding. While typically porphyrin N-H units are not involved in intermolecular bonds as they are “shielded” by the macrocyclic system, distortion may increase the accessibility to the porphyrin core. Notably, substituents on the periphery of the macrocycle can distort the molecule due to *peri* interactions. This forces the central N-H units into an outwards orientation, exposing them to acceptor molecules.



Objectives:

- Preparation and characterization of double-sided nonplanar picket-fence porphyrins.

Tasks:

- Synthesis of functionalized precursor aldehydes for porphyrin condensation reactions.
- Synthesis of highly substituted nonplanar porphyrins with functional groups for secondary stabilization of substrates.
- Spectroscopic and structural characterization of sad-distorted porphyrins.
- Spectrophotometric characterization of porphyrin-analyte binding.

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Chemistry, nAChRs and the brain

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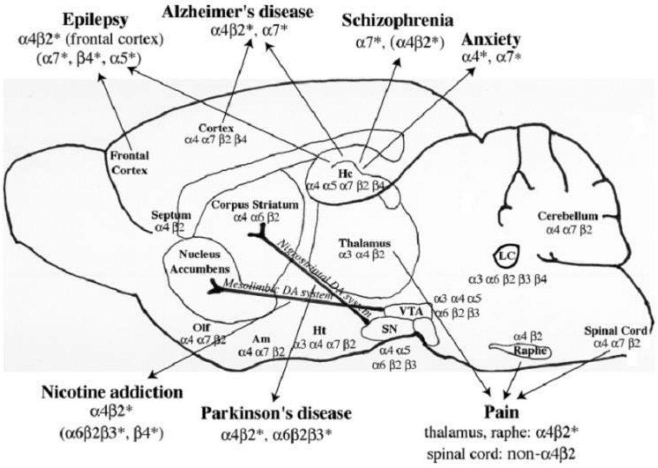
Research Project Description:

This project is concerned with developing new compounds that have the potential to mediate a number of cognitive disorders such as addiction, depression, ADHD and Tourette syndrome. Our lead structure is a compound that has been shown to reduce cravings in human subjects addicted to nicotine, cocaine and/or alcohol but it can be improved. The lead has also been shown to reduce self-administration of a wide variety of abused and addictive drugs in animal models. The overall aim of the project is to modify the structure to prepare more effective compounds that will be employed to probe the molecular mechanisms of addiction with the long-term aim of understanding the underlying neurochemistry and providing an effective treatment. The lead compound is a neuronal nicotinic acetylcholine receptor (nAChR) antagonist and these receptors have been strongly implicated in the process of addiction, a debilitating condition that causes huge suffering and financial drain on individuals and the state. The neuronal nAChRs are family of ion channels made up of 5 subunits, each of which is a 4-transmembrane protein. To date 12 neuronal sub units have been identified, 2 4 and 2-10 and some of their postulated roles are shown below. However, the precise roles of different subtypes in addiction, and the many other cognitive processes that they are thought to mediate, is poorly understood.

Note that this project will involve multi-step synthetic chemistry.



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Epilepsy, AMPA receptors and decanoic acid

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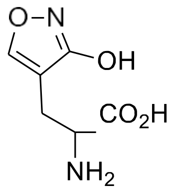
Research Project Description:

Epilepsy is a serious condition that results from a distortion of the usual balance of inhibitory and excitatory pathways within the brain. During a seizure excitatory activity dominates and this is mediated by glutamatergic pathways i.e. those employing glutamate as the key neurotransmitter. Of particular significance are the AMPA family of glutamate receptors. The AMPA receptors are a subset of glutamatergic ion channels that are selectively activated by α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA). Upon activation the ion channels allow the influx of sodium, potassium and occasionally calcium cations (depending on specific sub-type) causing a depolarisation of the neuronal membrane.

Current epilepsy drugs can provide relief of symptoms in many cases but a subset of patients suffer from mitochondrial or refractory epilepsy for which current treatments provide little, if any, relief. However, the ketogenic diet (high fat, adequate protein, low carbohydrate) so named on account of the production of high quantities of ketone bodies (acetone, hydroxyl butyric acid and acetoacetate) during fat metabolism has can reduce seizures dramatically in the case of refractory epilepsy. The MCT (medium chain glyceride) variant of the ketogenic diet (MCT-ketogenic) is particularly effective. The diet is rather restrictive in nature and far from balanced with a number of detrimental short and long-term consequences. Metabolic analysis of the patient on the MCT-ketogenic diet shows that high concentrations of decanoic acid are produced. Decanoic acid is an AMPA antagonist that reduces the number of seizures in mitochondrial epilepsy by preventing the (excitatory) depolarisation of neuronal membranes by preventing activation of the AMPA receptor.

To date, the development of drugs for mitochondrial epilepsy has been seriously hampered by the lack of suitable model for the disease. Fortunately, Prof. Mark Cunningham (School of Physiology, TCD) has recently developed a successful model.[1] The aim of the project is to work with Prof. Cunningham to develop novel derivatives of the simple decanoic acid structure to determine the factors associated with activity, with the long term aim of developing compounds to treat mitochondrial epilepsy effectively and without having to resort to the restrictive and problematic MCT-ketogenic diet.



α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA)

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School of Chemistry Senior Sophister Research Project 2021

Theoretical Study of Phase-Transfer Catalysts for Asymmetric Conjugate Additions of Cyanide

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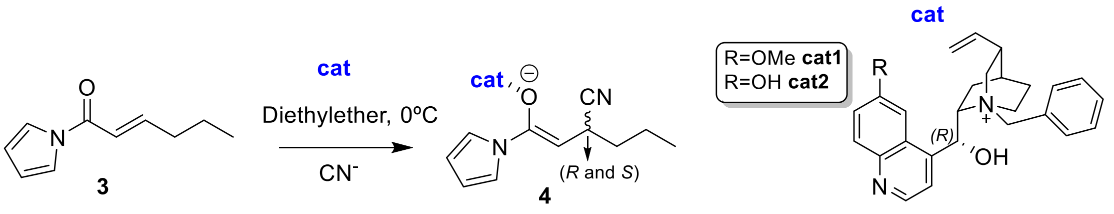
Research Project Description:

A wide variety of asymmetric transformations catalysed by chiral catalysts were developed for the synthesis of valuable organic compounds in the past several decades. Within asymmetric catalysis field, phase-transfer catalysis was recognized as a powerful method for establishing useful procedures for organic synthesis.

While the field of asymmetric organocatalysis is currently growing exponentially, an understanding of the mechanistic details involved in most of these reactions has often lagged far behind the pace of catalyst development, which in return retards rational catalyst design. Therefore, continuous efforts should be made toward the design and development of new catalysts classes, as well as understanding existing relationships between the structure of the catalyst and its ability to transfer stereochemical information.

Catalytic asymmetric cyanation of prochiral unsaturated compounds were extensively studied in recent years as their reaction products are considered highly desirable building blocks for pharmaceutical compounds. Here in, the mechanistic picture of the enantioselective conjugate cyanation of unsaturated ketone catalysed by a *Cinchona* alkaloid quaternary salt will be studied. An improved PTC derivative to the existing system is proposed in order to increase the enantioselectivity of a model reaction and therefore a theoretical study of the free-energy profile will be performed.



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Study of Tuneable Bioactive Anion Transporters

Dr. Cristina Trujillo (CT2)
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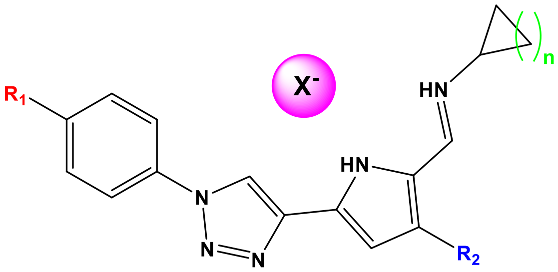
Research Project Description:

The development of supramolecular anionophores for transmembrane ion transport is driven by their potential utility as tools for studying ion transport processes and as therapeutics for diseases arising from mis-regulation of protein ion channels.

Significant effort has been devoted to designing mobile carrier systems with high anion transport activity in vesicles (particularly for chloride), and more recently, in cells. Transmembrane ion transport by synthetic anionophores is typically achieved using polar hydrogen bonding anion receptors. As with naturally occurring ion transporters, anion selectivity is crucial, and depends on the delicate balance between transporter anion binding selectivity and anion desolvation.

A theoretical study of the different non-covalent interactions established between anions and bioactive anion transporter molecules is proposed. An analysis of the anion-anionophore encounter and characterisation of the different interactions established are crucial to induce variations within the anion-transporter molecule to increase the affinity and therefore improve the anion transporter process.



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Physical, Computational and Materials Chemistry

Functionalisation of Electroactive Small Organic Molecules for Diagnostic Model Systems

Dr. Maria Daniela Angione (MDA1)
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Research Project Description:

Given the periodic emergence of new and old infections, and the pressing challenges from antimicrobial resistance and pandemic threats such as Ebola and Zika, modern, disease-relevant methodologies represent critical target for improving our knowledge of the dynamics of host-pathogen interactions in their natural environment. Although many traditional models provide valuable tools for studying the mechanism of action of drugs there is a pressing need to revisit cell culture assay systems, to develop new models, and innovative screening technologies that better recapitulate in vivo physiology. In this context, functional organic electroactive materials are showing significant advancement in the development of *in vitro* model systems as well as diagnostic and implantable devices. The capability of organic electronic materials, in fact, in conducting and processing both electronic and ionic (bio)signals, tightly coupled via electron-ion charge compensation [1-3], lays the ground for the development of multivalent tools with enhanced sensitivity. Moreover, organic electroactive molecules can be designed via synthesis [4] to possess desired physical and chemical properties, thus enabling the manufacture of bioelectronics devices and systems that exhibit desired flexibility, elasticity, and morphology, and with a surface chemistry, that promotes biocompatibility and stability over extended periods [5].

***Objectives*.-** Realisation of an electroactive organic film, ad-hoc chemically functionalised with bio-moieties such as glycans and membrane proteins. We will explore different functionalization approaches (i.e. direct chemical functionalization, physisorption/inclusion and plasma modification) to establish which strategies ensures a better recapitulation of the bio-moieties natural environment.
- Extensive surface and bulk chemical characterization of the system realized in order to investigating bio-moieties orientation, crowding and clustering. In addition, will be carried out an investigation into the electronic properties of the functional organic system, in order to determine the sensitivity of the novel material developed in probing disease-related ionic and electronic processes.

Outcomes. The student will acquire skills in processing and functionalization of small organic electroactive molecules with biomolecules, exploring different chemical and physical approaches. In addition, the student will be trained in electronic probing and electronic microscopies for the characterization of the electroactive material realized. The student will learn about interfacing biomolecules with organic systems, specifically they will gain insights into ionic and electronic transfer processes,

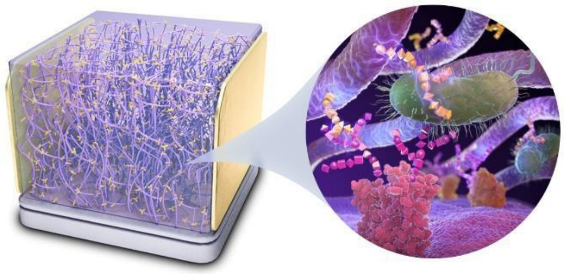

Figure 1: Representation of the functional electroactive system based on bio-functionalised small organic molecules in investigating host-pathogens interaction processes.

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2D TMD modified membranes for filtration Applications

Dr. Ramesh Babu (RB1)
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Research Project Description:

Membrane filtration is one of the versatile and rapidly growing technology for advanced separation and water treatment applications. Hence, it is always of special interest to improve surface/bulk membrane properties for achieving desired multi- functionalities. Recent trends on developing layer-stacked 2D nanomaterials-based membranes is exciting for its great mechanical and physico-chemical properties. Emerging 2D transition metal dichalcogenides, like liquid exfoliated MoS2 is holding greater potential in terms of nano-structural stability and water filtration capability than that of graphene oxide (GO), which has been reported to pose limitations in terms of fabrication complexity and membrane integrity towards pressure-driven water filtration applications.

By taking advantage of MoS2 having strong Van der Waals structure with stable/narrow inter-layer spacing and many other desired properties suitable for application in aqueous environments, it is proposed to develop and characterize scalable/tuneable exfoliated MoS2 nanosheets based polymeric membranes using approaches related to surface cross-linking or electrospinning methods. The overall aim of the project is to address the challenges in achieving fabrication scalability of MoS2 based membranes for filtration applications.

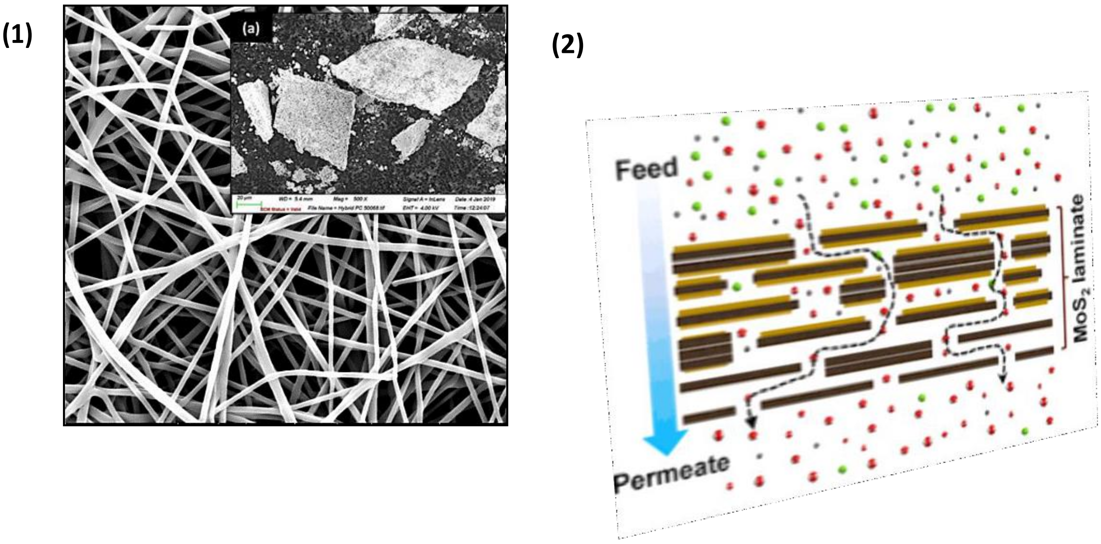

Figure (1) Surface morphology of electrospun nanofibrous membrane[1], (a-insert) exfoliated MoS2 doped ZnO (2) Scheme representing water transport through laminated MoS2 nanosheets fixed on membrane substrate[2]

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Investigating the performance of cross-flow electro membrane filtration using charge selective nanofiltration membranes

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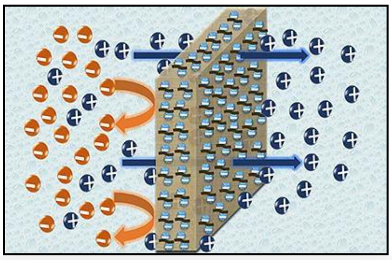
Research Project Description:

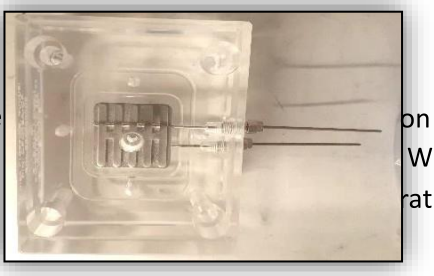
Pressure-driven membrane nanofiltration (NF) is known for its ability to separate solutes based on size exclusion and electrostatic repulsions. Because of NF membrane pore size and their charge properties, NF is promising process to separate low molecular weight compounds like divalent ions, heavy metals, sugars and so on, thus finding application ranging from food, dairy, pharmaceutical, effluent treatment and water purification among many. Yet, major limitation of NF exists in terms of achieving selective ion removal and susceptibility to fouling, which requires attention. Cross-flow electro membrane nanofiltration (CFEMF) process have the potential to conjugate the electrical field as an additional driving force to enable the charged molecules to move towards the oppositely charge electrodes. The synergistic combination of NF along with electric potential further helps in maintaining high productivity with reduced fouling.

This project aims on examining the performance of both commercially available ion-exchange membrane and indigenously developed surface charged/conductive NF membranes while separating ionic solutes of economic and environmental significance. The combined effects of electrical field, diffusion and hydrodynamic forces for solute permeation during CFEMF will be evaluated based on feed and NF membrane characteristics.

(1)



(2)



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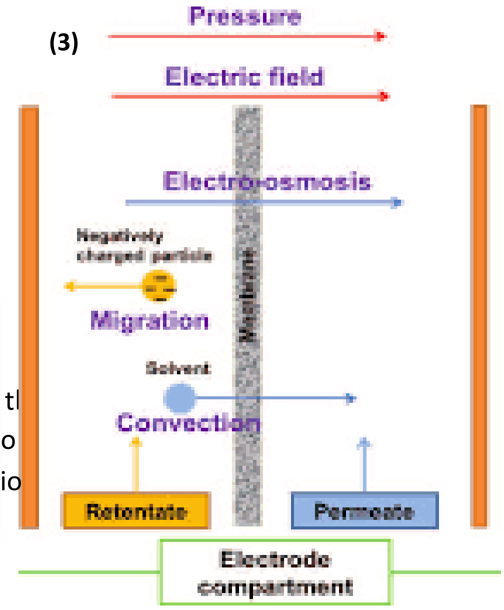

Figure (1) Sche … on tl
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References:

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School of Chemistry Senior Sophister Research Project 2021

The morphology and stability of nanocrystalline metal films at few nanometer thicknesses

Prof John Boland (JJB1)
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Research Project Description:

Metals are the most abundant elements and crucial in all aspects of everyday life: from structural and mechanical engineering to facilitating electricity transmission to forming the tiny wires that connect each and every electronic device. There is an enormous interest in producing metals with improved mechanical and electrical properties to reduce energy losses and increase for instance the battery life of hand-held devices. We are leading this effort by investigating the properties of nanocrystalline metal films[1] that are used to form the metal connections between individual transistors on a chip. The wires are sub-10nm, they are fragile and their ability to conduct charge diminishes as their size is reduced. Nanocrystalline metals are comprised of 20-50nm sized grains separated by grain boundaries. We have recently understood how grain boundaries can be exploited to enhance the stability of these films and this project will involve observing the evolution of the film structure as the thickness of the film is reduced by chemical etching. Specifically, this will entail a series of experiment to control the film thickness and then the use of atomic force and scanning electron microscopy to image the evolving surface structure and the subsequent thermal stability of the film. The latter measurement will be formed by determining the temperature that causes the film of ball-up on the substrate. The student will work as part of a team and training and mentoring will be provided throughout.

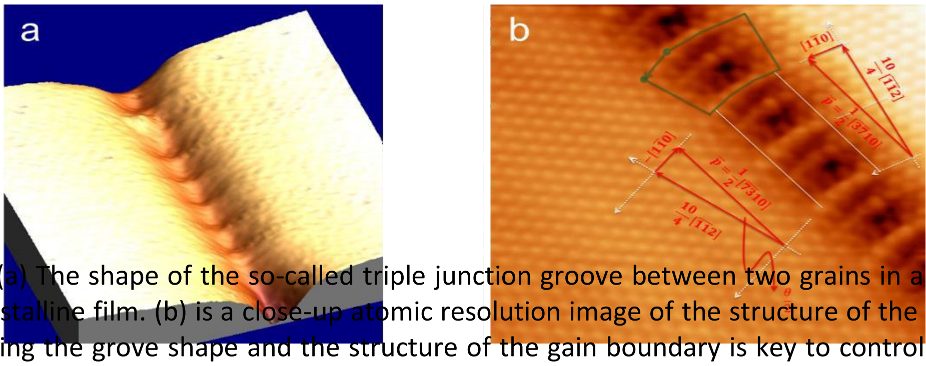

Figure: (a) The shape of the so-called triple junction groove between two grains in a copper nanocrystalline film. (b) is a close-up atomic resolution image of the structure of the groove. Controlling the grove shape and the structure of the gain boundary is key to controlling the electrical and thermal stability of the film

References

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The Degradation of Polymers in Water

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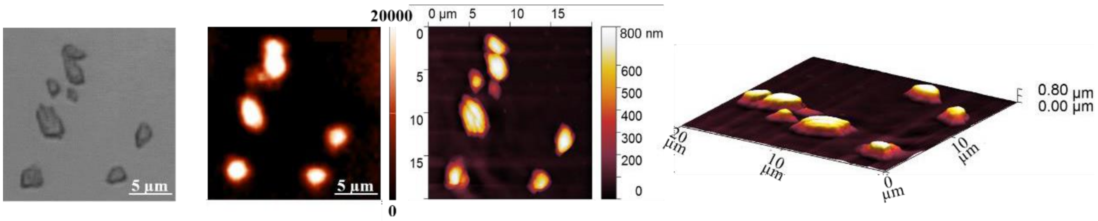
Research Project Description:

Globally, there is a significant dependence on plastic products in our everyday life, from kitchen appliances and smart technology devices to food packaging and storage. The high demand for plastic results in around 380 million tons being produced annually (*1*). Most plastics are non-biodegradable, but can break down into small fragments known as microplastics (MPs) due to chemical and physical processes such as hydrolysis, oxidation, radiation and mechanical actions such as friction, scratching and others (*2, 3*). MPs have become an increasing global concern (*3*) due to their potential risk to the environment and to human health (*4-6*)

Using Raman and atomic force microscopy (AFM) mapping, we have investigated the quantity and size distribution of the MPs released from many standard plastic products. We have found that typically millions of MPs and trillions of nano-plastic are released per litre of water in contact with the plastic. This project involves a study of the mechanism of plastic degradation in the presence of water. The student will be part of a larger team and will receive mentoring and training on a wide range of imaging technologies, experiment design and statistical methods to estimate particle numbers.



Characterization and quantification of polypropylene (PP) microplastics. (A) Optical microscopic image of particles released from BFBs under with 100x microscope objective. **(B)** The Raman mapping of the same region obtained by PP Raman bands of 2830-2870 cm^{-1}. The *color scale bar* indicates the intensity of the integrated spectral band in arbitrary units. **(C)** The AFM image of the same region to determine the morphology of released MPs. The *color scale bar* indicates the height of MPs. **(D)** 3D AFM topographic image.

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Sustainable materials for new energy technologies

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The interest in low-cost nanomaterials for electrocatalysis, has increased exponentially over the last few years. This results from the convergence of economic and societal demands for a more sustainable management of energy resources, with recent discoveries in the area of carbon materials for electrode applications. Electrochemical energy technologies such as fuel cells, metal-air batteries and water splitting are expected to play a key role in future energy solutions, however these technologies rely on the use of precious and/or scarce elements, thus posing severe limitations to the scale of their deployment due to cost and sustainability concerns. Replacement of scarce materials or significant improvements on the activity of current catalysts will be therefore necessary to ensure a cost-effective expansion of electrochemical conversion technologies. Low cost carbon materials and oxides of earth-abundant elements are interesting candidates for replacing or enhancing electrocatalysis of critical reactions for the energy economy.

The objectives in this project are to investigate the synthesis and properties of low-cost nanomaterials in electrocatalysis of reactions that are important for electrochemical energy conversion, e.g. the oxygen reduction and evolution reactions. Synthesis methods for disordered oxides and carbon nanostructured materials will be used to tailor catalytic activity in electrocatalysis while fundamental studies with diagnostic redox probes will be used to complement the understanding of these nanomaterials.

Tasks: You will prepare carbon and/or oxide nanostructured materials using one or more methods among ultraspray continuous flow, hydrothermal synthesis and/or batch surface modification of commercial nanomaterials. Figure 1 shows examples of electroactive materials prepared in our group using these methods.[1,2] You will study the structure and properties of these new materials using a combination of spectroscopic (e.g. XPS, infrared), physical (e.g. contact angle) and electrochemical techniques (e.g. voltammetry, hydrodynamic techniques).

Skills: You will acquire expertise in surface characterization techniques for determining e.g. surface composition/chemistry, surface free energy, and in methods for establishing catalytic performance with standard redox probes (LSV, EIS) and with energy-relevant species (e.g. O_2, H_2O_2).

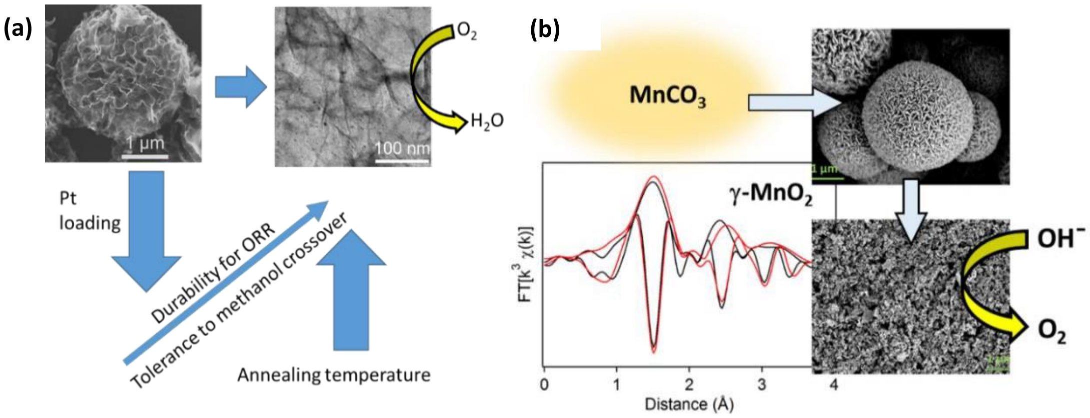

Figure1. (a) Carbon nanostructured microspheres for stable and methanol tolerant Pt-nanoparticle catalysis; these materials catalyse the oxygen reduction for methanol fuel cells [1]. (b) Nanostructured MnOx microspheres obtained via hydrothermal synthesis; these materials catalyse the oxygen evolution reaction that is essential in water splitting [2].

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Responsive Photonic Crystal Structures

Dr. Larisa Florea (LF1)
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Research Project Description:
This project will utilise cutting-edge fabrication technologies, combined with stimuli-responsive materials to fabricate photonic crystal sensors. Photonic crystals are periodic assemblies, based on natural or synthetic structures, which can control the propagation of light, and therefore the reflected wavelength of light. To date, the fabrication of optical sensors, based on photonic crystals has followed two distinct routes: via advances in 1) materials or 2) structure design.[1] The former has relied on the deposition of functionalised nanomaterials, via sedimentation, spin coating, or vertical deposition, to form nanostructured responsive films.[2] The latter has relied on top down fabrication such as e-beam lithography, nano-imprint lithography or etching. This project aims to combine advances in highly-specific stimuli-responsive materials[3-5], with high-resolution 3D fabrication. In this context, structures will be fabricated from stimuli-responsive materials, using direct laser writing by 2-Photon Polymerisation[6] (Figure 1).

This project will involve investigating the effect of incorporating stimuli-responsive structures in the photonic crystal structures (during or post fabrication) and characterisation of the obtained structures by UV/Vis, Raman and FT-IR spectroscopy.

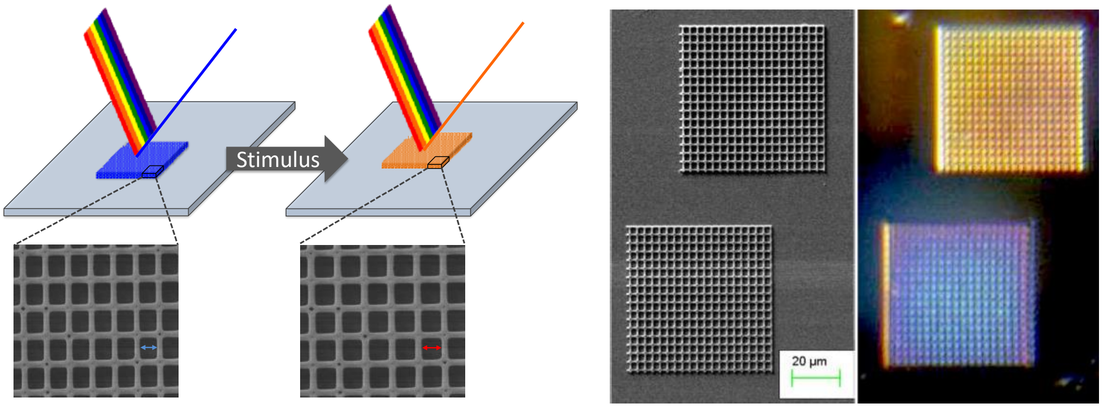

Figure 1. Photonic crystal sensor. (Left) Diagram depicting the working principle of the sensor. The sensor consists of stimuli-responsive 3D structure fabricated by direct laser writing. (Right) SEM and reflection microscopy images of the 3D structures fabricated by direct laser writing.

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Stimuli-responsive Hydrogel Structures

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Research Project Description:

Hydrogels are three-dimensional, hydrophilic polymer networks, capable of water uptake. By incorporating molecular switches in their structure, stimuli-responsive hydrogel actuators can be developed, that respond to a variety of stimuli, such as light (Fig. 1), electric or magnetic fields, or a change in the local environment.[1-5] The aim of this research will be to investigate the feasibility of using responsive hydrogels as micro-machines, capable of doing mechanical work in response to chosen stimuli. Moreover, new functionalities such as sensing, and switchable uptake and release of molecular guests, will also be incorporated in the same hydrogel material, in order to create synthetic units with biomimetic features.

During this project the student will explore several bioinspired microstructures based on stimuli-responsive hydrogels. The development of new synthetic protocols for functional monomers based on molecular switches and polymer optimisation will prove integral to this investigation. A variety of polymerization approaches will be investigated to control the nature of the hydrogel and to best translate the molecular change to a macro response. The project will involve synthesis and characterisation of the molecular switches using a variety of spectroscopic techniques (NMR, FT-IR, UV-Vis and fluorescence spectroscopy), the optimization of the fabrication process and complete characterization of the hydrogel structures (optical microscopy, SEM).

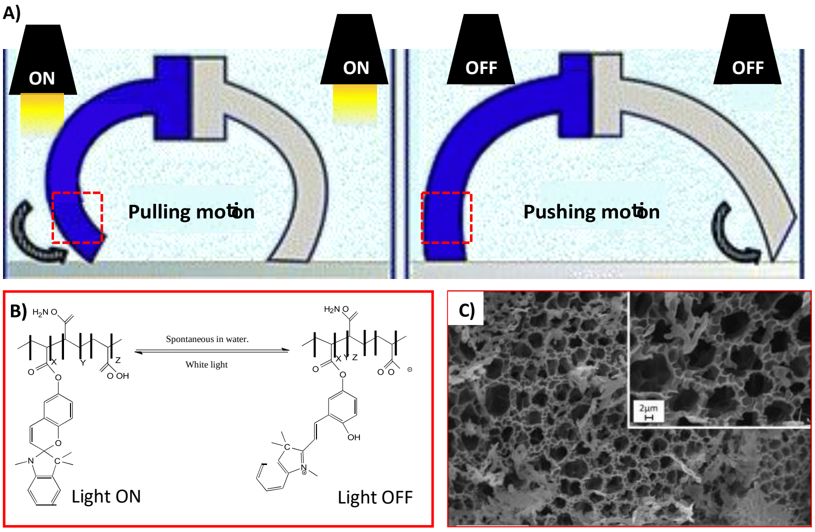

Figure 1. A) Schematic illustration of a photo-actuated hydrogel micro-walker; B) Chemical structure of the polymer used for the fabrication of the photo-actuated hydrogel micro-walker; C) SEM image showing the high porosity of the hydrogel material.

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Mechanistic Study on the Na-Mediated Ferration for Regioselective Functionalisation of Fluoroarenes via C–F Bond Activation

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Research Project Description

Recent experimental work by Hevia *et al.*[1] has shown that pairing iron bis(amide) Fe(HMDS)$_2$ (HMDS: bis(trimethylsilyl)amine) with Na-(HMDS) allows to form a new sodium ferrate base [(dioxane)$_{0.5}$NaFe(HMDS)$_3$] which enables regioselective mono- and di-ferration (via direct Fe–H exchange) of a wide range of fluoroaromatic substrates under mild reaction conditions. Furthermore, using an excess of the sodium ferrate base at 80ºC was found to trigger a remarkable cascade reaction with 1,3,5-trifluorobenzenes, inducing the collective twofold C–H/threefold C–F bond activations, where each C–H bond is transformed to a C–Fe bond whereas each C–F bond is transformed into a C–N bond (see Figure). By trapping several ferrated intermediates, it has been proposed that the synchronised Na/Fe cooperation plays a key role in these transformations, although the exact mechanism and the role of the two elements are yet to be discovered.

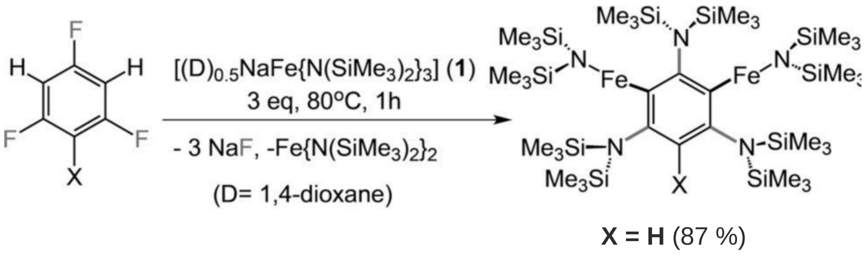

Figure. Two-fold C–H/three-fold C–F activation processes of 1,3,5-trifluorobenzene.

The proposed project will be conducted in the Computational Catalysis and Energy Materials group, led by Prof. Max García-Melchor, and in close collaboration with the experimental group of Prof. Hevia. In particular, it will involve the use of density functional theory methods within the Gaussian09 software to elucidate the reaction mechanism of the C–F bond activation process in 1,3,5-trifluorobenzene mediated by the sodium ferrate base. With this aim, the student will propose a reaction pathway(s) starting from the ferrated compound in positions 2, 4 and 6, and model the main reaction intermediates and transition states involved. After elucidating the reaction mechanism, the student will perform an in-depth molecular orbital analysis of the rate-determining step to shed light on the main role of Na and Fe. With these theoretical insights, the student should be able to suggest experiments to fine-tune the sodium ferrate base or propose new metal-ferrate bases that favour C–F activation.

References

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Mechanistic Study on the Na-Mediated Ferration for Regioselective Functionalisation of Fluoroarenes via C–H Bond Activation

Prof. Max García-Melchor (MGM2)
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Research Project Description

Recent experimental work by Hevia *et al.*[1] has shown that pairing iron bis(amide) $Fe(HMDS)_2$ (HMDS: bis(trimethylsilyl)amine) with Na-(HMDS) allows to form a new sodium ferrate base $[(dioxane)_{0.5}NaFe(HMDS)_3]$ which enables regioselective mono- and di-ferration (via direct Fe–H exchange) of a wide range of fluoroaromatic substrates under mild reaction conditions. By trapping several ferrated intermediates, it has been proposed that the synchronised Na/Fe cooperation plays a key role in these transformations, although the exact mechanism and the role of the two elements are yet to be discovered.

The proposed project will be conducted in the Computational Catalysis and Energy Materials group, led by Prof. Max García-Melchor, and in close collaboration with the experimental group of Prof. Hevia. In particular, it will involve the use of density functional theory methods within the Gaussian09 software to elucidate the reaction mechanism of the Na-mediated ferration of pentafluorobenzene, shown below. With this aim, the student will propose a reaction pathway(s) and model the main reaction intermediates and transition states involved in it. After elucidating the reaction mechanism, the student will perform an in-depth molecular orbital analysis of the rate-determining step to shed light on the main role of Na and Fe. With these theoretical insights, the student should be able to guide the fine-tuning of the sodium ferrate base or to suggest new metal-ferrate bases for further experiments.

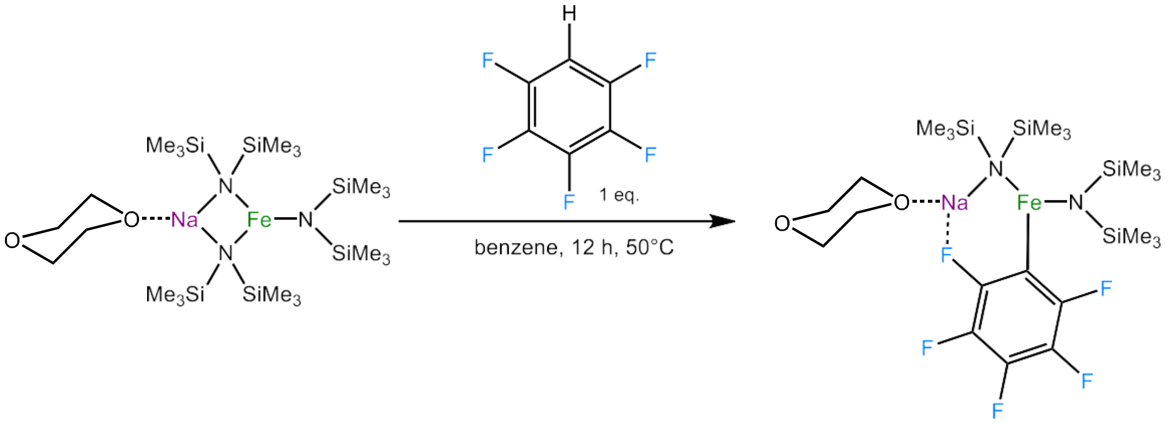

Figure. Na-mediated ferration of pentafluorobenzene by the sodium ferrate base $[(dioxane)_{0.5}NaFe(HMDS)_3]$.

References

2. Maddock, L. C. H.; Nixon, T.; Kennedy, A. R.; Probert, M. R.; Clegg, W.; Hevia, E. *Angew. Chem. Int. Ed.* **2018**, *57*, 187.

Monitoring chemical transformations on plasmonic nanoparticles by Raman spectroscopy

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Metal nanoparticles can act as nanoscale antennas allowing them to funnel energy carried by light into nanoscale volumes on their surfaces. This funneling of light into nanoscale volumes can result in enhanced light-matter interactions in these regions. Consequently, these particles are of great interest for use in a new generation of photocatalysts and optoelectronic devices.[1]

In this project, arrays of metal nanostructures fabricated by electron-beam lithography will be used to enhance photocatalytic processes. We have previously shown that metal nanoantennas illuminated at their resonant wavelength can emit electrons.[2] Moreover, in recent work, we have shown that they can cause siloxanes such as HSQ to cross-link in specific regions on their surface that are determined by the antenna material and geometry, as shown in figure 1. In this work, Raman spectroscopy will be used to monitor chemical transformations on individual plasmonic nanostructures while illuminated at their resonant wavelength by a visible or near-infrared laser. This work will support the development of new catalyst materials and help improve our understanding of energy conversion processes in these systems.

During the project the student will have the opportunity to further develop their understanding of spectroscopic processes as well as surface science and catalysis. They will also learn about electron microscopy and nanofabrication by working with a postgraduate student and regularly discussing results with Dr. Hobbs.

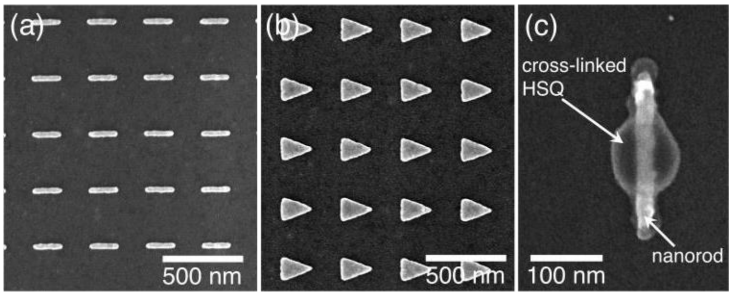

Figure 1. (a,b) Scanning electron microscope (SEM) images of Au nanorods and nanotriangle antennas fabricated by electron-beam lithography. (c) SEM image of localized region of cross-linked HSQ at the centre of a Au nanorod after illumination with a laser that is spectrally matched to the surface plasmon resonance.

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Synthesis of heterostructured plasmonic nanoparticles

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When metal nanoparticles are illuminated at certain characteristic frequencies, collective oscillations of conduction electrons called surface plasmons are excited resulting in amplification of electromagnetic fields on their surface. The amplified fields can drive localized chemistry at these surfaces, including for example, the dissociation of precursor compounds. The dissociation of precursor compounds on the surface of these particles will enable the synthesis of heterostructured plasmonic nanoparticles suited to applications in photocatalysis as well as providing new routes to nanostructure synthesis.[1,2]

In this project, nanoparticle arrays fabricated by electron-beam lithography[3] will be used to drive dissociation of precursor compounds in solution phase. The student will characterize the optical properties of the nanoparticle arrays and perform experiments to dissociate precursor compounds on their surfaces. They will work with other group members to characterize the synthesized material by electron microscopy and spectroscopy. In this project, the student will investigate the use of different semiconductor precursor compounds for the synthesis of germanium, zinc oxide or titanium dioxide nanostructures suited to applications in photodetection and photocatalysis respectively.

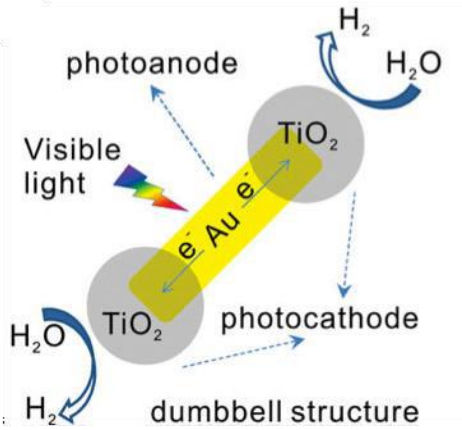

Figure 1. Schematic of a Au-TiO_2 heterostructured nanoparticle operating as a catalyst for hydrogen evolution.[1] In this work, plasmon-enhanced fields will be used to drive precursor decomposition in the desired locations to produce heterostructures with morphologies suited to catalyst and photodetector applications.

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Bonding and Repulsion in Hydrogen Donor-Acceptor Pattern Recognition

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Research Project Description:
The accepted role of hydrogen-bonding in nucleotide recognition has been questioned by Kool at al. [1] who have suggested that complementary shapes, mimicking nucleotides, may alone be sufficient for discrimination (Fig. 1). Seddon and Evans however have questioned this view [2]. It is not necessarily a binary choice; the role of hydrogen donor-acceptor patterns in nucleotide recognition may be regarded as twofold, serving to bind associating complementary pairs, while simultaneously opposing non-complementary associations [3].

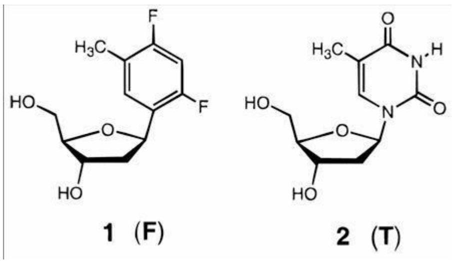

Figure 1. Difluorotoluene (F), a Nonpolar Isotere for Thymine (T) [2].

The evolutionary theoretician Eörs Szathmáry has developed a model for assessing the biological fitness of alternative alphabets with a view to explaining the particular genetic alphabet employed by nature [4]. While the results were interesting, the interactions energies he employed were very approximate. In this project Szathmáry's model will be revisited, adapted where necessary, and using improved estimates of interaction energies. The project will involve Quantum Chemical calculations and a small amount of programming (though Excel may suffice).

The objective of the project will be to gain further quantitative insight into the relative importance of the repulsive and attractive components in nucleotide recognition, and thereby better understand the factors underlying the particular composition of the genetic alphabet (A, T, C and G) and as well as possible alternatives. The project should inform us on the robustness of Szathmáry's model and his conclusions.

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Tautomeric Instability and the Composition of the Nucleotide Alphabet

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Research Project Description:

Piccirilli *et al* [1] have demonstrated the chemical feasibility of incorporating novel base pairs into the genetic alphabet (Fig 1). The question therefore arises as to why nucleic acid sequences are assembled from the four bases G, C, A and U as opposed to an alternative or larger alphabet.

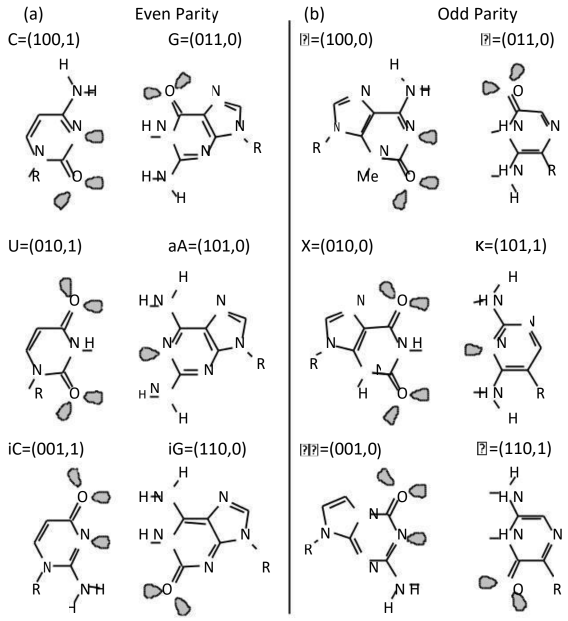

Figure 1. Potentially viable nucleotides divided by parity (a) the even-parity subset and (b) the odd- parity subset.

Some potential members of the genetic alphabet are rendered non-viable by reason of tautomeric instability. For example, the donor/acceptor pattern in iG is unstable, in contrast to that of G. The project will employ a variety of *ab initio* and semi-empirical quantum–chemical approaches to explore the underlying basis of the instability and will attempt to identify stable alternatives to A, T, C and G.

1. J. A. Piccirilli, T. Krauch, & S. E. Moroney & S. A. Benner et al., “Enzymatic Incorporation of a New Base Pair into DNA and RNA Extends the Genetic Alphabet”, *Nature*, Vol. 343, 33-37, 1990.

http://dx.doi.org/10.1038/343033a0

Development of ultra-thin energy storage devices based on two- dimensional nanomaterials

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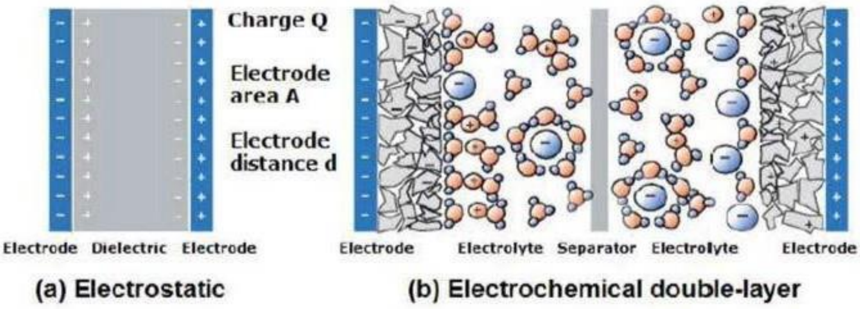
Research Project Description:
Energy storage will be more important in the future than at any time in history. Climate change and the decreasing availability of fossil fuels require society to move towards sustainable and renewable resources. As a result, we are observing an increase in renewable energy production from sun and wind, as well as the development of electric vehicles or hybrid electric vehicles with low CO_2 emissions. Because the sun does not shine during the night, wind does not blow on demand and we all expect to drive our car with at least a few hours of autonomy, energy storage systems are starting to play a larger part in our lives. Supercapacitors store energy electrochemically, using reversible adsorption of charges of an electrolyte onto two porous electrodes and the formation of the so-called electric double layer at an electrode/electrolyte interface (see figure below)[1]. We plan to use thin layers of conductive two-dimensional nanomaterials[2-4] and unexploited ultrasonic deposition technologies to produce more efficient, ultra-thin, flexible supercapacitors. The work will involve processing on large scale equipment, followed by detailed microscopical characterization.



(a) Electrostatic (b) Electrochemical double-layer

Figure: Schematic of (a) a parallel-plate electrostatic capacitor ; (b) an electrochemical supercapacitor.

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Doping Cu_2O – towards low cost photovoltaic cells.

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Research Project Description:
The sun offers an immense amount of free and clean power, which we have not yet begun to seriously exploit. Metal oxides are ideal candidates owing to their combination of low cost and high stability in aqueous solutions. Unfortunately the optical band-gaps of many metal oxides generally lie outside the visible range (> 3 eV) making them bad for solar applications. Despite immense effort, attempts to reduce the band-gaps of active oxides such as TiO2 through dyes, doping or co-doping have not succeeded in providing a viable material.

Cu2O was the first material for which a patent was granted for a photovoltaic material but despite its historical importance, Cu2O never gained great interest. With a band gap of 2.1 eV the maximum efficiency predicted from the Shockley-Queisser limit [1] is around 20% with the current interest stemming from its natural p-type conducting properties [2] and potential for very low cost photovoltaic devices [3]. To generate the most efficient device, a homojunction cell [figure 1] in which both n-type and p-type Cu2O are present would need to be fabricated, [3] although currently no viable way of creating (through doping) n-type Cu2O has been found [4].

In this project we will use density functional theory to examine the defect chemistry of Cu2O to determine (i) if improved p-type properties can be generated (e.g. by N doping) and (ii) if simple doping can generate n-type Cu2O (e.g. by Cl doping). In addition we will look at the native defects (Cu and O vacancies, Cu and O interstitials) to determine if these defects can form in opposition to the doped defects.

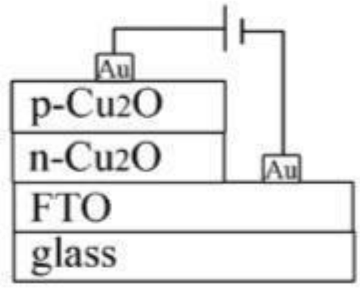

Figure 1. Schematic of a Cu_2O homojunction photovoltaic cell.

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The impact of grain boundaries on the ionic conductivity of doped CeO_2

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Research Project Description:

The grain boundaries within multi-crystalline materials give rise to structural discontinuities which result in specific GB structures, potential non-stoichiometry and the segregation of point defects, all of which can significantly alter the macroscopic properties [1]. As a consequence, grain boundaries and interfaces can control the properties of materials and hence they are vital to understanding and optimising their performance. Despite this, there is little understanding of the structure and even less on the effects of these interfaces on materials properties due to the inherent complexity of the issues and limited experimental techniques.

We have recently developed a method of predicting the structure of tilt grain boundaries using sophisticated polarizable forcefields and applied this to CeO_2 [2] and demonstrated the segregation of oxide ion vacancies to the interface resulting in enhance 2D diffusion (figure 1). This project seeks to determine the impact of dopant segregation to the boundary on the ionic conductivity. Such data is important in understanding the impact of material processing in multi-crystalline materials for the electrolyte of solid oxide fuel cells.

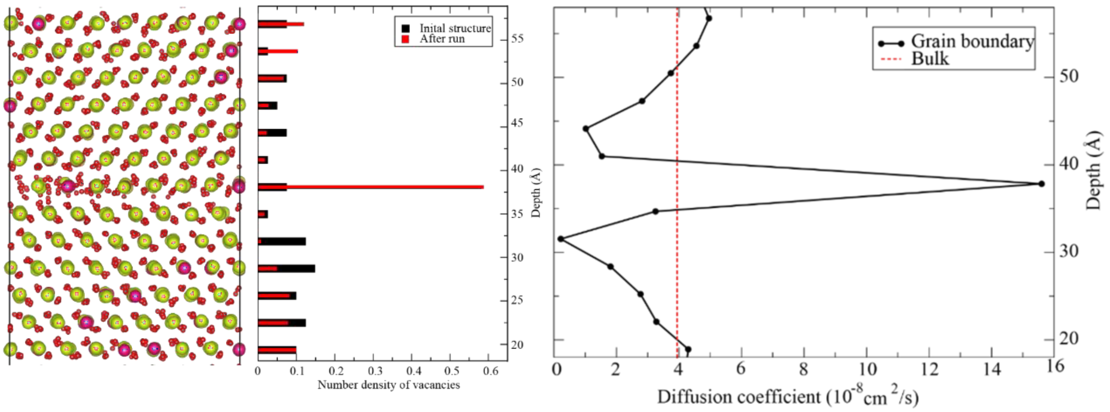

Figure 1 Results from a Molecular dynamics simulation of the $\Sigma 3(111)$ GB of $Ce_{0.9}Sm_{0.1}O_{1.95}$. a) Structural model, b) oxygen vacancy distribution before and after annealing and c) resulting ionic diffusion parallel to the interface.

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