75th Irish Universities Chemistry Research Colloquium

17/18th June 2024, Trinity College Dublin

run annually under the aegis of the **Institute of Chemistry of Ireland**

SCHEDULE AND BOOK OF ABSTRACTS

Contents

Welcome to the 75th IUCRC Colloquium!

After the successful event last year at U Galway, the organising committee has worked to maintain the structure and give the opportunity to all final year PhD students to give an oral presentation. We have 38 Talks in two parallel sessions and a Poster Session with 65 Posters. The latter will be followed by a reception where we expect that all attendees can socialise and get to know each other.

We also have four prominent Plenary Speakers, Prof. Serena Cussen, Prof. Batchelor-McAuley, Prof. Dorota Gryko and Dr. Kielmann, each representing different areas of research and expertise and this year's ICI PG awardee Dr. Ellen Faye.

The next pages have the Schedule, List of Presenters and Titles and the List of Abstracts. We hope you have a good time at the Colloquium and get some good ideas for your Chemistry research. But first we set out formally our Dignity and Respect Responsibilities.

Our Responsibilities. As the Organising Committee we:

- want everyone to enjoy the Colloquium and feel able to contribute
- will not share any communication on anyone's personal circumstances/experience
- will treat everyone with dignity and respect and conduct ourselves in a respectful manner
- will be kind to each other and not insult or put down other Colloquium attendees
- will ensure that all communication, online or in person, will be appropriate for a professional audience and considerate of people from different cultural backgrounds
- will contribute to discussion with a constructive and positive approach
- seek actively to exclude harassment including (but not limited to): offensive verbal comments, exclusionary jokes, deliberate intimidation, stalking, following, harassing photography or recording, sustained disruption of discussions, inappropriate physical contact and unwanted sexual attention.

Your Responsibilities. As a Colloquium Participant, you agree to:

- foster equal participation
- maintain privacy/confidentiality
- not tolerate bullying, harassment, or discrimination
- respect people's identities & experiences
- engage with kindness and respect
- keep communication professional
- consider diverse cultural backgrounds
- contribute constructively.

Organising Committee: Prof. Mathias O. Senge, Prof. Larisa Florea, Prof. Richard Hobbs, Dr. Karolina Urbanska, Dr. Jason Delente, Dr. Sinead Boyce, Ben Power, Manting Mu.

Much appreciation to our Sponsors!

We are very grateful to our Sponsors without whom the Colloquium would not have been possible:

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- Royal Society of Chemistry (Republic of Ireland Local Section)

75th Irish Universities Chemistry Research Colloquium

17th & 18th June 2024, Trinity Biomedical Sciences Institute

June 17th		
Room	L2.15 Tercentenary	B1.15 St. Quek
08:30 - 09:15	Registration	
09:15 - 09:30	Conference opening Prof. Graeme Watson	
09:30 - 10:30	***Prof. Serena Cussen*** ***Chair: Graeme Watson***	
10:30 - 11:00	Coffee break / *poster setup*	
11:00 - 13:00	**Organic Synthesis** ***Chair: Nessan Kerrigan***	**Materials for Energy** ***Chair: Mercedes Vazquez***
	Evan Judge (UCC)	Keith Sirengo (ATU)
	Aoibheann O'Connor (UCD)	Ryan Walden (ATU)
	Fionn McNeill (UCD)	Eva Naughton (UCD)
	Dara Curran (UCD)	Filippo Pota (TCD)
	Adam O'Connell (UCD)	Irthasa Aazem VS (ATU)
	Kathryn Yeow (UCD)	Karlijn Hertsig(TCD)
13:00 - 14:30	Lunch break *local outlets*	
14:30 - 15:15	***Prof. Chris Batchelor McAuley*** ***Paula Colavita***	
15:15 - 17:05	**Organic Synthesis** ***Chair: Mathias Senge***	**Functional Materials** ***Chair: Richard Hobbs***
	Dandan Lin (UCD)	Amit Goswami (ATU)
	Arlene Bonner (UCD)	Annaël Sort-Montenegro (TCD)
	Rachel O'Sullivan (UCD)	Abhijit Wickramasinghe (TUD)
	Kate Donaghy (UCD)	Amrutha Augustine (TCD)
	Hong Ann Gan (TUS)	Luisa Lavelle (TCD)
17:05 – 17:15	ICI YCN - AGM	
17:15 - 19:00	Poster session	
19:30 - 22:00	Social evening (Pav TCD)	

June 18th		
Room	L2.15 Tercentenary	B1.15 St. Quek
09:00 - 10:00	***Prof. Dorota Gryko*** ***Chair: Prof. Senge***	
10:00 - 11:20	**Medicinal Chemistry** ***Chair: Diego Montagner***	**(Bio)Materials Discovery** ***Chair: Larisa Florea***
	Conor Shine (RCSI)	Manting Mu (TCD)
	Shubhangi Kandwal (TCD)	Keelan Byrne (MU)
	John Connolly (RCSI)	Cian Clarke (TCD)
	Mairead Gallagher (TUD)	Maria Byrne (UCD)
11:20 – 11:50	Coffee break	
11:50 - 13:10	**Medicinal Chemistry** ***Chair: Roisin O'Flaherty***	**(Bio)Materials Discovery** ***Chair: Suresh Pillai***
	Darren Beirne (MU)	Mariana Diniz (UL)
	Connie Sigurvinsson (TCD)	Enrico Spoletti (UL)
	Clara Evans (MU)	Athira Tomy (MU)
	Grace Lawler (TUS)	Usaid Azhar (ATU)
13:10 - 13:30	Ellen Faye – ICI PG Awardee	
13:30 - 14:15	***Dr. Marc Kielmann*** ***Chair: Mathias Senge***	
14:15 - 14:30	Closing and Prize Awards Prof. Pat Guiry	

List of Oral Presenters and Seminar Titles

L2.15 Tercentenary 17th June 2024			
11:00-13:00 Organic Synthesis			
Evan Judge	UCC	α-Diazo-β-keto sulfonamides: Design and Reactivity	O1
Aoibheann O'Connor	UCD	A New Paradigm for the Asymmetric Diels-Alder Reaction	O2
Fionn McNeill	UCD	Enantioselective Synthesis of Sterically Hindered α-Allyl-α-Aryl O-Heterocycles *via* Decarboxylative Asymmetric Allylic Alkylation	O3
Dara Curran	UCD	Phosphine-Mediated Hydrolytic Etherification of Alcohols and Aromatic Aldehydes	O4
Adam O'Connell	UCD	Biocatalytic Routes to Complex N-Heterocycles	O5
Kathryn Yeow	UCD	Biocatalytic Cascades for the Synthesis of Therapeutic Iminosugars from Monosaccharides	O6
B1.15 St. Quek 17th June 2024			
11:00-13:00 Materials for Energy			
Keith Sirengo	ATU	Exploring the effect of aging ether-based electrolyte on the cycle life of lithium metal batteries	O7
Ryan Walden	ATU	Effects of Non-thermal Plasma Treatments on Commercial Fabrics for Application in Textile Triboelectric Nanogenerators	O8
Eva Naughton	UCD	Heterogeneous catalysts for promotion of Artificial Photosynthesis	O9
Filippo Pota	TCD	Carbon-encapsulated metal N-doped porous materials: A promising architecture for electrocatalytic hydrogenation of biomass derivative organics	O10
Irthasa Aazem VS	ATU	Ceramic fillers incorporated Polyvinylidene Fluoride (PVDF) and Nylon-6 Polymer nanocomposites for Self-powered Triboelectric Nanogenerators (TENGs)	O11
Karlijn Hertsig	TCD	Towards Sustainable Nanomaterials: Greener Routes to Quantum and Carbon Dots	O12
L2.15 Tercentenary 17th June 2024			
15:15-17:05 Organic Synthesis			
Dandan Lin	UCD	An Electrochemical Oxidation Prins-Type Cyclisation sequence for the Construction of 1,3-Oxazinan-2-ones via *N*-Acyliminium Ions	O13
Arlene Bonner	UCD	The Integration of Continuous Flow Technology with Strained Cyclic Systems	O14
Rachel O'Sullivan	UCD	The Development of Novel Ferrocenyl Compounds *via* Acid-Mediated Transformations and the Diastereoselective Synthesis of a Novel Indene	O15
Kate Donaghy	UCD	Stereoselective Synthesis of α-Glycosides	O16
Hong Ann Gan	TUS	Laccase Oxidation Studies	O17
B1.15 St. Quek 17th June 2024			
15:15-17:05 Functional Materials			
Amit Goswami	ATU	Superhydrophobic candle soot based anti-icing coatings through environmentally friendly synthesis methods	O18

Annaël Sort-Montenegro	TCD	Electro-guided Soft Micro-vehicles: From Polymer Microstructures to Ionic Liquid Droplets	O19
Abhijit Wickramasinghe	TUD	Zeolite EMT Entrapped Ruthenium Polypyridine Materials for Photocatalytic Degradation of Pollutants	O20
Amrutha Augustine	TCD	Nanocomposite Photoresists for Structural Coloration	O21
Luisa Lavelle	TCD	Direct Laser Writing of Complex 3D Metal Nanoparticle Patterns within Polymer Microstructures for Photothermal Micro-Actuators	O22
L2.15 Tercentenary 18th June 2024			
10:00-11:20 Medicinal Chemistry			
Conor Shine	RCSI	Antibacterial Polymers Mimicking Antimicrobial Peptides	O23
Shubhangi Kandwal	TCD	Discovery of small molecules blocking a key binding site in SARS-CoV-2 nsp3 protein	O24
John Connolly	RCSI	Design and synthesis of novel antimicrobial peptides replacing amino acids with conventional small molecule antibiotics producing an amalgamation of a peptide mimetic/conjugate system	O25
Mairead Gallagher	TCD	Antibiotic Metabolites: Synthesis, Characterisation, and Assessment of their Role in Antibiotic Resistance Development	O26
B1.15 St. Quek 18th June 2024			
10:00-11:20 (Bio)Materials Discovery			
Manting Mu	TCD	Novel Proton Shuttling Mechanism in Pd(II)-Catalyzed Wacker-type Oxidation	O27
Keelan Byrne	MU	Mechanistic Insight into Alkali-Metal Mediation of Styrene Transfer Hydrogenation: A DFT Study	O28
Cian Clarke	TCD	A Python-Based Workflow for the Automated Generation of Molecular Libraries	O29
Maria Byrne	UCD	Multifunctional Luminescent Silica Nanoparticles for Applications as Biological Probes and Delivery Agents	O30
L2.15 Tercentenary 18th June 2024			
11:50-13:10 Medicinal Chemistry			
Darren Beirne	MU	Pt(IV) – Tyrosine Kinase Inhibitors: Potent dual-modal conjugates	O31
Connie Sigurvinsson	TCD	Naphthalimides Exhibiting Aggregation Induced Emission for Bioimaging Applications	O32
Clara Evans	MU	Developing Novel Re(I) Tricarbonyl Complexes as Antimicrobial and Anticancer Agents to Combat Drug Resistance	O33
Grace Lawler	TUS	Integrating efficacy with characterisation: pioneering a novel target profile for topical antifungal solutions	O33
B1.15 St. Quek 18th June 2024			
11:50-13:10 (Bio)materials Discovery			
Mariana Diniz	UL	Unravelling the effects of solvents in the crystal nucleation of griseofulvin	O35
Enrico Spoletti	UL	Xanthines sulfate salts from tea and chocolate: a solid form landscape investigation	O36

Athira Tomy	MU	Non-enzymatic sensing platform for *N*-Acetyl Neuraminic Acid based on electrodeposited boronic acid film on glassy carbon electrodes	O37
Usaid Azhar	ATU	Development and Characterisation of Poly(catecholamine) Surface Coatings	O38

List of Poster Presentations

Giulia Ferrari	MU	Pt (IV)-DEVD-doxorubicin conjugates as dual action prodrugs for selectivity treatment of osteosarcoma	P1
Michele Coi	TCD	High valent first-row transition metal halides complexes for oxidative halogenation of saturated hydrocarbons	P2
Suncica Sukur	MU	Development of Biocompatible Graphene Oxide-Based Magnetic Nanoplatforms for Targeted Drug Delivery	P3
Joshua Thorogood	TCD	Synthetic Magnesium Tetrapyrroles for Mechanistic Studies of Photosystem II	P4
Ashwini Mishra	UCD	Utilisation of waste products for the construction of alkenes	P5
Emily Collins	UCC	Development of Synthetic Routes to Novel Sulfur-Based Antivirals	P6
Amy Twomey	UCC	Exploring Metal-Organic Frameworks as Catalysts in the Synthesis of Methyl Acrylate from CO_2	P7
Michelle O'Driscoll	UCC	Tackling Antimicrobial Resistance *via* Novel BDSF Quorum Sensing Inhibitors	P8
Gangireddy Reddy	UCC	Investigation of a synthetic route to aromatic Resolvins	P9
Karina Chan	RCSI	Development of Pt-PROTACs to degrade Pt-binding Proteins	P10
Rebecca O'Keefe	UCC	Enantioselective Intramolecular C-H Insertions of α-Diazosulfonates	P11
Aylin Ahmadinia	TCD	Development of green-based coatings with anti-corrosion properties	P12
Éabha McMahon	UCC	Intermolecular C-H Insertion Reactions of α-Diazosulfones	P13
Luke Glennon	MU	Electrochemical Detection of Ornidazole by means of Copper-Iron nanoparticles and Carbon Black-modified electrode	P14
Colm Ennis	MU	Bifunctional Layered Double Hydroxide Electrocatalysts for Water Splitting	P15
Rachel Lynch	UCD	Carbon Dioxide Utilisation for Construction of High Value Carboxyl-Containing Organic Products	P16
Fiona Kinsella	UCC	Asymmetric Synthesis Using Transaminases as Biocatalysts	P17
Oscar Kelly	TCD	Model Compounds for the Investigation of Electrostatic Effects in Photosynthetic Pigments	P18
Olga Clavilier	MU	Carbon-negative construction materials from a biorefinery	P19
Léa Diebold	MU	Towards tumour theranostics: hypoxia activation as a tool for therapy and diagnostics	P20
Aoife Newman	MU	Printable Mediated Glucose Biosensor Development for Wearable Devices	P21
Chloe Stapleton Jackson	MU	Characterisation of a Polymer-Enzyme Composite Biosensor for Brain Extracellular Glucose	P22
Marcin Szydło	UCD	Development of a Redox-Neutral Wittig Reaction Catalysed by Phosphorus	P23

Mouna Hind Laiche	RCSI	Design, synthesis and screening of novel prenylated chalcones as optimised anti-cancer agents	P24
Brian Durkan	RCSI	Desulfurative Fluorination of Alkyl Phenyl Sulfides via Bromonium Catalysis	P25
Valentina Magno	TUD	Investigation of the protein corona of gold nanoparticles as a possible biomarker for glycan based diagnostics	P26
Keane McNamee	MU	Platinum black and miniaturised electrodes for neurochemical monitoring	P27
Conor Cassidy	MU	Nickel boride/transition metal dichalcogenides as potential bifunctional electrocatalysts for water splitting	P28
Katie McHugh	UG	Dual Delivery of Anti-Cancer Drugs using Metal-Organic Framework	P29
Sebastian Pim	RCSI	Observing bioorthogonal macrocyclization in live cell nuclear membranes using on/on fluorescence lifetime microscopy	P30
Niamh Lehane	UCD	Asymmetric Synthesis of α-Aryl Stereocentres in Dihydroquinolinones *via* DAAA and DAP	P31
Orlagh Beggs	TCD	High-Valent Iron Halide Oxidants for Hydrocarbon Oxidation	P32
Alexandra Lapiy	MU	Glutathione Sensor Development with the aid of Electrosynthesised Nanogold	P33
Yiran Luo	MU	Ultrasensitive Detection of Sulfamerazine with CeO_2 mixed Spherical Spinel $ZnMn_2O_4$ combined with WS_2 Sheets	P34
Freya Ritterling	TCD	Rigid Hydrocarbon Isosteres as Linkers in Porphyrin Dyads for Sensing Application	P35
Sreedhanya Pallilavalappil	ATU	Electrochemical Evaluation of FeCo Oxide and Ag/FeCo Oxide Nanocomposites Derived from Prussian Blue Analogues for Oxygen Evolution	P36
Joseph Monahan	MU	Utilisation of Surface-Modified Transition Metal Dichalcogenides as Unconventional Antimicrobial Agents	P37
Adam T. McCormack	MU	Continuous flow synthesis of Black Hole Quenchers	P38
Eleanor Windle	UCD	Structurally Dependent DNA Disruption of Phthalocyanine Aggregates	P39
Marilia Dalla Benetta	MU	Room Temperature Modification of Carbon Cloth for Water Splitting	P40
Ciara McEvoy	MU	Enhancing Pyrazolopyrimidinone Cytotoxicity against Glioblastoma using Cold Atmospheric Plasma (CAP)	P41
Niamh O'Shea	TCD	The Synthesis of Mechanically Interlocking Molecules using the btp [2,6-bis(1,2,3-triazole-4-yl)pyridine] motif	P42
Bláithín Rawson	TCD	Host-Guest Chemistry of Napthalene Diimide based Macrocycles	P43
Jordan Loughlin	MU	Novel Squaratide Based Glycoconjugates (SBG's) to Selectively Target Cancer Cells	P44
Yingru Zhou	DCU	Can carbon dots be used as nanocarrier scaffolds?	P45
Christine Coffey	UCD	Towards Phosphorus Cations as Main Group Catalysts	P46
Marianna Zolyomiova	DCU	Development of a Portable and User-Friendly Enclosed System with Smartphone Camera Detection for Identifying Microplastics in Urban Water Runoff	P47

Oana Popa	UCD	Stereoselective 1,2-*cis*-glucosylations	P48
Mandapati Bhargava Reddy	UCD	Visible-light-induced carbosulfonylation of alkynes	P49
Zarah McGeever	DCU	Synthesis of Gamma-Lactones from Epoxides and Ketenes	P50
Shaista Jabeen	ATU	Tungsten Carbide: A High-Efficiency Electrocatalyst for Hydrogen Evolution Reaction (HER)	P51
Martina Tuberti	TUD	Computational studies, design and synthesis of Tau protein fragments, to explore a potential role in Alzheimer's disease	P52
Sophie Maguire	TCD	Exploration of synthetic strategies for the development of non-planar atropisomeric porphyrins	P53
Liam Cribbin	TCD	C-C bond formation in a sterically demanding environment	P54
Soumoshree Sengupta	TCD	BODIPY-anthracene dyads as versatile photosensitizers	P55
Bodhayan Biswas	UCD	Towards automated synthesis of monosaccharide building blocks and applications in oligosaccharide synthesis	P56
Amravati Gode	UL	New insight into organic solid solutions using low-frequency phonon analysis	P57
Yekaterina Tskhe	TCD	pH-Responsive Hydrogel Micro-Actuators	P58
Aoife Donohoe	TCD	Bio-Inspired Photonic Actuators	P59
Emma Nolan	DCU	Lunar Regolith and Anti-Adhesion Nanostructures	P60
Meabh Kennedy	DCU	Mechanobactericidal Polymer Surfaces for Medical Devices –Synthesis and functionalisation of poly(2-allyloxymethyl-2-ethyltrimethylenecarbonate) (PAOMEC)	P61
Teodora Faraone	TCD	Composite polymer microstructures fabricated via direct laser writing for structural colouration and analyte sensing	P62
Mary Flood	UCD	Instability of RNA Mitigated by Reversible Ribose 2'-OH Acylation	P63
Ciara Tobin	DCU	Fabrication of Electrospun Membranes for Water Filtration	P64
Daniel Molloy	UCD	Degradation of Perfluorooctanoic Acid by Plasma-Assisted Catalysis in a DBD Reactor	P65

Plenary Speakers

Fine-tuning synthesis to optimise energy storage: insights from advanced characterisation

Professor Serena Cussen

School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

A global transition to net zero will require innovations in materials manufacture that increase efficiency and reduce consumption, all while continuing to meet demand and satisfy application needs. Sustainable manufacturing processes that address the challenges of resource efficiency and multi-level optimization could reduce manufacturing resource to just the amount required. Here, I will present some of our recent work on the development of microwave chemistry approaches to materials for energy storage as well as our future plans to move from batch synthesis to continuous processes. For example, our observations for garnet electrolyte batch microwave-synthesis (leading candidate materials for safer next-generation solid-state batteries) have demonstrated that these processing techniques can reduce reaction times and temperatures; the rapid, homogeneous microwave heating affords a single-phase high ionic conducting material. We can also target faceted cathode particles, such as high nickel content cathodes for next-generation Li-ion batteries, as well as lower cost cathodes such as olivine materials. The addition of microwave heating can afford materials with less defects, which impacts subsequent battery performance. I will also showcase some of our recent development of in situ muon spin relaxation measurements that allow us to interrogate ion diffusion across electrode-electrolyte interfaces. This talk will highlight how careful synthetic design can enable performance and a comprehensive analysis provides greater insight into materials properties.

Biography

Serena Cussen (née Corr) is Full Professor of Materials Chemistry at University College Dublin. She obtained her BA and PhD degrees in Chemistry from Trinity College Dublin, before going on to carry out postdoctoral research at University of California Santa Barbara with Professor Ram Seshadri.

Serena's research focuses on understanding the synthesis-structure-function interplay in materials for electrochemical energy storage. Her group are particularly interested in determining strategic routes to functional materials which afford control over crystal chemistry, particle size and particle morphology and deepening our understanding of the impact this has over properties. Recipient of the RSC Journal of Materials Chemistry Lectureship (2017), the ISIS Science Impact Award (2021) and the RSC Interdisciplinary Prize (2023), Serena is deeply committed to career sustainability, early career mentoring, the promotion of women in STEM and public outreach. A former member of the RSC's Materials Division Council, she has contributed to the RSC's Equity in Publishing group (contributing to the recent "Is publishing in the chemical sciences gender biased?" report) and was featured in the International Women's Day report "The Chemical Ladies".

From Energy to Sustainability: Studying Reactions at the Single Particle Scale

Chris Batchelor-McAuley

Trinity College Dublin, Ireland

McAuleyGroup.net

Biography: Chris was recently appointed as an Assistant Prof. in TCD and moved to Ireland in 2022. Prior to this he was a OMS Fellow at the University of Oxford. Over the years Chris' research has ranged from Fundamental to Applied, having worked on projects such as quantifying the pH of fetal blood through to developing electron transfer theory and creating ultra-low noise electronics for measuring electrochemical reactions at the single nanoparticle scale. This work has led to him publishing 200 articles and 6 patents and he has been cited in total over 5000 times (WoS 2023, excluding self-citations). In 2012 Chris co-authored the textbook "Understanding Voltammetry: Problems and Solutions" and he recently co-edited an issue of the review journal Current Opinion in Electrochemistry.

Abstract: Why study materials at the single particle scale? From an analytical standpoint this approach is important; by investigating objects one-at-a-time, we can start to understand and quantify heterogeneity in a sample. We can ask ‘are all nanoparticles in a sample equally active’? However, beyond this direct analytical interest the approach has more general applications, for example, in marine monitoring it allows us to ask ‘how much of the biogenically precipitated calcite in a seawater sample is bound to phytoplankton’? This is a key question in understanding the oceanic carbon fluxes. This single particle approach also raises interest from a physical chemistry standpoint. As we look at things on an increasingly small scale does the chemistry or reactivity of the material change? The kinetics of a solid/solution interfacial reaction are generically intimately linked with mass-transport, usually diffusion, occurring in the vicinity of the interface of interest. How can this altered mass-transport change the apparent reactivity of the material?

This seminar will begin by looking at how, for solution phase interfacial reactions, the rate determining step can change as a function of the particle size. Changing the size of a particle can radically alter a reaction pathway for this class of reactions. Can this change in reactivity influence a material’s nanotoxicity? Next, the issue of surface heterogeneity[1] will be considered and the extent to which we can correlate changes in a surface’s activity with its structure explored. Finally, the seminar will turn to consider two experimental cases[2,3] and outline recent examples of how reactions have been studied on the single particle scale.

References

[1] Wong, Rachel, et al. "Electrochemical Heterogeneity at the Nanoscale: Diffusion to Partially Active Nanocubes." The Journal of Physical Chemistry Letters 13 (2022): 7689-7693.
[2] Yu, Wenmiao, et al. "Characterising Porosity in Platinum Nanoparticles." Nanoscale 11 (2019): 17791-17799.
[3] Yang, Minjun, et al. "Opto-Electrochemical Dissolution Reveals Coccolith Calcium Carbonate Content." Angewandte Chemie 133 (2021): 21167-21174.

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Current research interests
Photochemistry, Co-catalysis, carbene chemistry, vitamin B_{12} chemistry and catalysis, and vitamin B_{12} as a delivery vehicle

Education

2000-2008: Habilitation, Institute of Organic Chemistry, PAS, Poland

1994-1997: PhD in Organic Chemistry, Institute of Organic Chemistry, PAS, Poland

(Supervisor: Prof. Janusz Jurczak)

1989-1994: M.Sc., with distinction, Warsaw University, Chemistry Department, Poland

Academic career
2015-present: Professor, Institute of Organic Chemistry, PAS, Warsaw, Poland.

2009-2015: Research group leader at the Institute of Organic Chemistry, Poland

2007-2007: visiting researcher at the University of Texas at Austin, USA, J. L. Sessler (2007), **porphyrinoid chemistry**

1998-2002: Postdoctoral Researcher, North Carolina State University, USA, (Supervisor: Prof. J. Lindsey)

She has published 120 scientific papers published in top-class scientific journals, including: Journal of the American Chemical Society, Angewandte Chemie International Edition, Chemical, Nature communications, Chemical Communications, 11 reviews and 5 book chapters. Her works have been cited almost 5,499 times (without self-citations, Google Scholar).

Awards:

1. Wojciech Świętosławski Award of the Polish Chemical Society, for outstanding achievements in the field of chemistry, chemical technology, and related sciences 2023
2. Award of the Minister of Science and Higher Education for Outstanding Achievements in science in 2019
3. Maria Curie Prize, for "The discovery of new biological properties of porphyrins in the fight of nosema' 2019
4. Award of the Director of the Institute of Organic Chemistry PAS for Scientific Achievements in 2018, 2019, 2020, 2021
5. Award of the Prime Minister of the Polish Government in 1998 for the Ph.D. thesis

Bioinspired reactions enabled by porphyrinoids

Dorota Gryko

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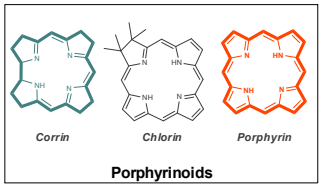
"Look deep into nature, and then you will understand everything better."

Albert Einstein

Porphyrinoids, also known as *the pigments of life,* are a class of naturally occurring organic dyes. They play key roles in crucial processes that support life - oxygen transport (hem), electron transport (cytochrome c), photosynthesis (chlorophyll a), and synthesis of DNA (vitamin B_{12}). Following nature, we have been exploiting the potential of these compounds in catalysis.

Vitamin B_{12} - catalysis has been successfully translated into the laboratory.[1-2] The advantage of using *vitamin B_{12} as a catalyst lays in the complete stability of the central cobalt ion and by the definition it is nontoxic*. It has also been well documented that the reaction mechanism usually follows a radical pathway, bringing a new dimension to this already interesting field.[2] Along this line, we have developed new vitamin B_{12}-catalyzed reactions involving reduction of Co(III) to Co(I) or Co(II) and subsequent reactions with electrophiles or radicals. Vitamin B_{12} derivative unusually catalyzes a new olefinic sp^2 C-H alkylation reaction with diazo reagents as a carbene source, acylation of activated olefins, alkylation of strained molecules.[3-5] We have also proved that *porphyrinoids are valuable photoredox catalysts that can be activated with both blue and red light*.[6]

These key findings emphasize the unique feature of porphyrinoids as catalysts to achieve something unachievable with other methodologies or to find a greener approach.



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1. Chemistry and Biochemistry of B_{12}; Banerjee, R., John Wiley & Sons, Inc, 1999.
2. Giedyk M.; Gryko D.; *Chem Catal.,* **2022,** 2, 1534; Wdowik, T., Gryko, D. *ACS Catal.* **2022**, *12*, 6517.
3. Ociepa, M.; Wierzba, A. J.; Turkowska, J.; Gryko, D. *J. Am. Chem. Soc.* **2020**, *142*, 5355.
4. Potrząsaj, A.; Musiejuk, M.; Chaładaj, W.; Giedyk, M; Gryko, D. *J. Am. Chem. Soc.*, **2021**, *143*, 9368.
5. Potrząsaj, A.; Ociepa, M.; Chaładaj, W.; Gryko, D. *Org. Lett.,* **2022**, 24, 2469.
6. Rybicka-Jasińska, K.; Shan, W.; Zawada, K.; Kadish, K. M.; Gryko, D. *J. Am. Chem. Soc.* **2016***, 138,* 15451.

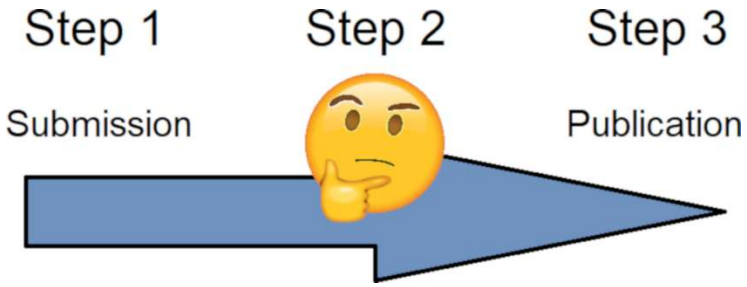
Insights into a journal editor's tool kit

Dr. Marc Kielmann

Beilstein Institut

In the past, editorial processes at scientific journals were thought of as a black box, where manuscripts are received as input on one side and publications are produced as output on the other. In this metaphor, the internal workings of the black box are not completely transparent, and therefore they are not fully understood by authors. Today, in order to be compliant with publishing standards and to meet the requirements of the scientific community, this is far from the truth. Scientific publishing has undergone years of transformation, which has resulted in more openness and transparency. Consequently, most reputable publishers communicate previously undisclosed or vague information more openly, such as journal metrics, editorial policies, and details about the manuscript workflow. However, there are still unwritten rules, tricks of the trade, and best practices that when incorporated can improve an author's chance of seeing their manuscript published.

The goal of this talk is to offer some practical advice for future authors and to foster curiosity in scientific publishing. The presentation is intended to be interactive, providing curated insights into an editor's tool kit while allowing plenty of time for discussion throughout. At the same time, the audience is invited to ask the questions they are most interested in and to share their own experiences from an author's point of view.



Biography

Marc Kielmann studied Chemistry (B.Sc.) and Medicinal and Natural Product Chemistry (M.Sc.) at the Leibniz Universität Hannover, working with Prof. Andreas Kirsching and Prof. Holger Butenschön.

After that, he successfully pursued his Ph.D. studies in the group of Prof. Mathias O. Senge at Trinity College Dublin, working on methods development and the synthesis of nonplanar porphyrins for use as organocatalysts and sensors.

Subsequently, he stayed as a EU-funded Postdoctoral Researcher with Prof. Senge, acting as liaison for the multinational research collaboration INITIO.

Marc joined the Beilstein-Institut as Scientific Editor in 2020 and is currently Managing Editor of the *Beilstein Journal of Organic Chemistry*. His interests include the ethics of science and open access publishing, which he has addressed in various talks and a panel discussion.

ICI Postgraduate Award Lecture

Nucleoside and Oligonucleotide Modification for Targeting DNA Damage Repair

Ellen M. Fay and Joanna F. McGouran

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The exonuclease SNM1A is a key enzyme involved in the repair of interstrand crosslinks, a highly cytotoxic form of DNA damage.[1] As cells depleted in this enzyme show increased sensitivity to certain chemotherapeutic agents,[2] SNM1A is a potential target for treating cancers that have developed resistance to traditional chemotherapeutics. However, SNM1A and other enzymes of this class are poorly understood as there is a lack of tools available to enable their study.

SNM1A facilitates DNA repair through the hydrolysis of the phosphodiester backbone. The active site of SNM1A contains two metal ions that are key to its catalytic activity. This work elaborates on previous results from the McGouran Group which identified that nucleosides and oligonucleotides, incorporating metal-binding groups, can successfully target the metal ions in the SNM1A active site. Initially, nucleoside modification was explored through the evaluation of novel carboxylate-rich nucleoside analogues for their ability to target SNM1A.[3] The ability of modified oligonucleotides to target SNM1A was also examined through the generation of a series of triazole-modified oligonucleotides, incorporating metal-binding groups, for targeted inhibition of SNM1A.[4] The investigation extended to the evaluation of a series of oligonucleotides featuring alternative backbones for their affinity for SNM1A.

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4. Fay, E. M.; Newton, A.; Berney, M.; El-Sagheer, A. H.; Brown, T.; McGouran, J. F., Two-Step Validation Approach for Tools To Study the DNA Repair Enzyme SNM1A. *ChemBioChem* **2023**, e202200756

Biography: Dr. Ellen M. Fay completed her BA (Mod) in Chemistry in Trinity College Dublin in 2019. During her undergraduate degree, she undertook her final year research project under the supervision of Prof. Joanna McGouran. Ellen was awarded a Government of Ireland Postgraduate Scholarship from the Irish Research Council and returned to the McGouran Group in September 2019 to pursue a PhD focusing on the development inhibitors and probes targeting DNA damage repair enzymes. Alongside her research, Ellen engaged in extensive outreach activities, promoting science to a wide range of audiences. She has travelled to over 30 schools across Ireland as a leader for Current Chemistry Investigators workshops, run by Dr John O' Donoghue. Ellen completed her PhD in April 2024 and is now working as Technical Officer in the School of Chemistry, Trinity College Dublin.

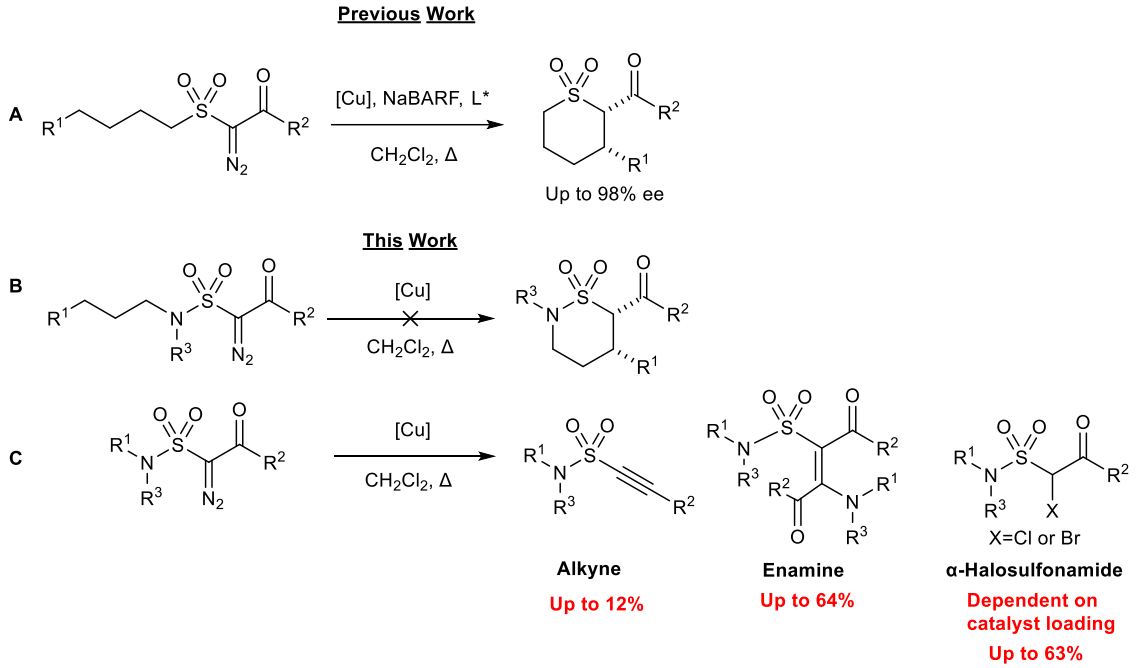
Abstracts Oral Presentations

α-Diazo-β-keto sulfonamides: Design and Reactivity

Evan Judge, Anita Maguire and Stuart Collins

School of Chemistry, University College Cork, College Road, Cork

A key challenge in synthetic organic chemistry is the formation of new carbon–carbon bonds in a controlled manner that ensures efficiency, cost effectiveness and control of 3D shape or stereochemistry. A powerful tool in a synthetic chemist's toolbox is the C–H insertion reaction. In recent years in the Maguire team, a plethora of research has been undertaken in developing novel C–H insertion pathways utilising copper catalysts which are more sustainable than alternative carbenoid sources.[1-3] Our group have demonstrated that a range of tetrahydrothiopyrans-*S*,*S*-dioxides may be synthesised from α-diazo-β-ketosulfones with excellent enantiocontrol (**A**).[1,2] The objective of this study is to establish if the copper mediated intramolecular C–H insertion could be extended to α-diazo-β-keto sulfonamides leading to sultams with good enantiocontrol (**B**).



Interestingly, the α-diazo-β-keto sulfonamides do not follow the same mechanistic pathway as that of the α-diazo-β-ketosulfones. Instead, a number of intriguing products and novel reaction pathways can be realized (**C**). The formation of a series of alkynes, enamines and α-halosulfonamides has been observed with the outcome dependent on the catalyst employed.

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A New Paradigm for the Asymmetric Diels-Alder Reaction

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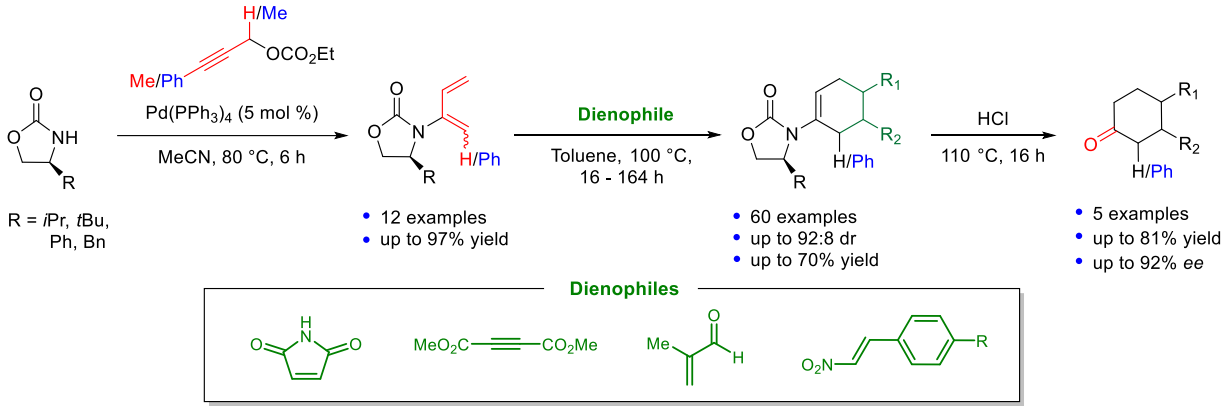
Centre for Synthesis & Chemical Biology, University College Dublin, Belfield, Dublin 4

The Diels–Alder (DA) reaction has been extensively developed and refined to become one of the most powerful methods to create carbon–carbon bonds in organic chemistry.[1][2][3] The asymmetric variation of the DA reaction was first investigated more than 50 years ago, and continues to see further development in the 21st century. Reportedly, the least investigated approach to the asymmetric DA reaction is the development and subsequent use of chiral dienes, as opposed to chiral catalysts and/or dienophiles.[4] The application of a chirally modified diene, as well as dienes containing an amido or amino group, is lacking in the literature.[5]

A catalytic method to prepare a library of chiral 2-amido-1,3- and 2-amido-1-phenyl-1,3-dienes from a range of oxazolidinones is reported. This palladium-catalysed carbon-nitrogen bond-forming reaction provides the corresponding chiral amido-dienes in moderate to excellent yields (12 examples, up to 97% yield). The resulting chiral amido-dienes are employed as novel dienes in DA reactions (60 examples, up to 70% yield, up to 92:8 dr). Hydrolysis of the DA products to cleave the oxazolidinone chiral auxiliary reveals a range of chiral cyclic ketones (5 examples, up to 81% yield, up to 92% ee) with XRD analysis providing key structural insights and confirming their stereochemistry.



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Enantioselective Synthesis of Sterically Hindered α-Allyl-α-Aryl O-Heterocycles *via* Decarboxylative Asymmetric Allylic Alkylation

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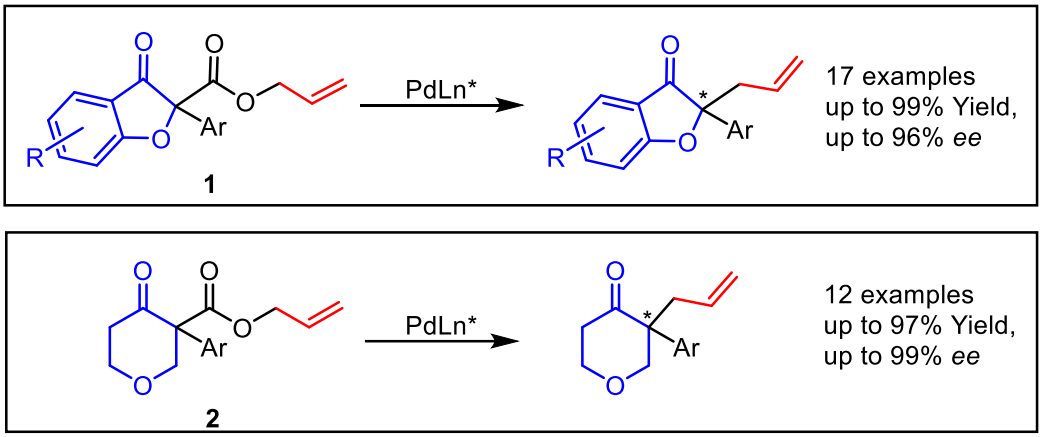
Oxygen-containing heterocycles are a common motif found in natural products and biologically active compounds. Additionally, quaternary α-aryl stereocenters are found in nature and have been shown to have interesting properties. Recent efforts with certain O-heterocycles have focused on the installation of aryl groups at the α-position to generate sterically hindered quaternary stereocenters.[1,2] These products can be accessed from the Pd-catalysed decarboxylative asymmetric allylic alkylation (DAAA) of α-aryl β-keto allyl esters. Although this methodology has been previously limited to small alkyl chains or functionalities distant from the reactive centre, the Guiry group has already extended the scope to other α-aryl containing substrates *via* the use of aryllead reagents to install the bulky groups on the reactive center before applying to catalysis.[3]

This project has focused on the utilisation of DAAA with two different O-heterocycles: benzofuran-3(2*H*)-ones (**1**)[4] and tetrahydro-4*H*-pyran-4-ones (**2**). The steps towards the synthesis of the model substrate in each case is described along with the optimisation and scope of the DAAA reaction for both, each demonstrating high yields and high enantioselectivities.



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Phosphine-Mediated Hydrolytic Etherification of Alcohols and Aromatic Aldehydes

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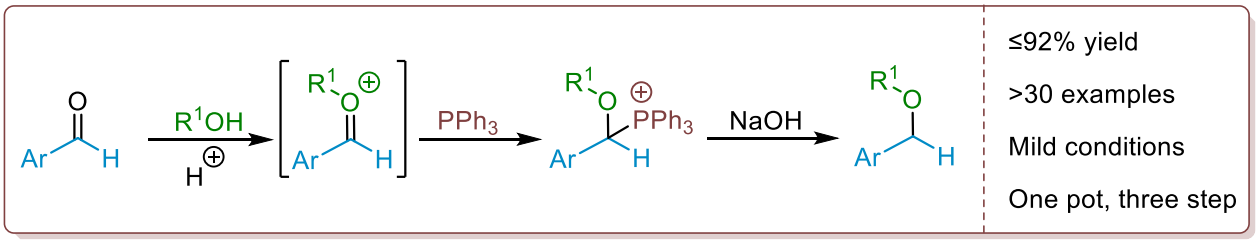
Ethers are among the most ubiquitous of pharmacophores in medicinally relevant drug molecules and, consequently, establishing sustainable routes to their syntheses is of the utmost importance.[1, 2] Classical methods for synthesising dialkyl or alkyl aryl ethers are known to have poor functional group tolerance due to the requirement of strongly basic reaction conditions and hence it has often been necessary to conduct ether syntheses in the early stages of a synthetic route to a drug.[3, 4] Furthermore, previous methods are reliant on the use of alkyl halides as electrophiles, the production of which results in generation of large quantities of halogenated waste through both the reactions used to directly produce the required alkyl halides and the prior processes used to produce the reagents required for such reactions.[5, 6]



In this project we propose a new direct formation of ethers from aromatic aldehydes and alcohols. This is attractive because both alcohols and aldehydes are naturally abundant, can be sustainably derived from biomass and are generally readily available. It has been found that the key intermediate in the formation of benzyl ethers can be obtained in a simple one step reaction. Subsequent phosphonium salt hydrolysis yields the desired benzyl ethers in up to 92% yield. This methodology provides an alternative means of accessing ethers in a chemoselective manner with high functional group tolerance that overcomes current limitations of other modern routes to ethers, whilst obviating the use of alkyl halides.

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Biocatalytic Routes to Complex N-Heterocycles

A. O'Connell, M.B. Haarr and E. O'Reilly

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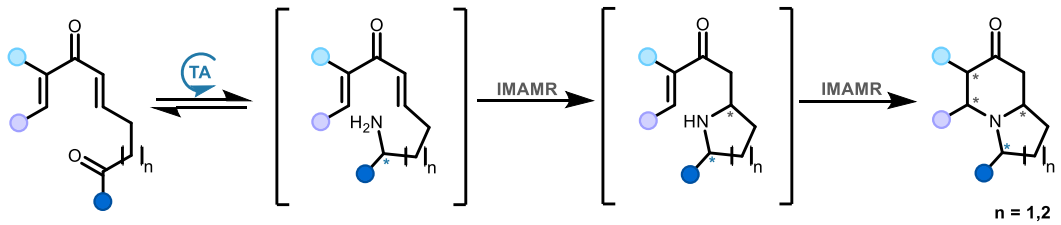
In recent years, biocatalysis has provided synthetic organic chemists with a new catalytic "toolbox" capable of performing novel chemistry in an efficient and sustainable manner.[1,2] Enzymes, with their unparalleled regio-, chemo-, and stereoselectivity, offer unprecedented opportunities for innovation and the opportunity to explore novel methodologies, one example being the ability to trigger subsequent reactions following an enzymatic transformation.[3,4] When targeting N-heterocyclic compounds, installation of a chiral amine moiety is often the initial and logical choice. There has been a number of enzymes used for the asymmetric induction of optically pure amines, with one of the most prominent being ω-transaminase (TA) enzymes.

Building upon previous work carried out in our group,[5] we proposed implementing a biocatalytically induced double intramolecular aza-Michael reaction (DIMAMR) for the formation of both quinolizidine- and indolizidine-containing structures, starting from suitably designed bis-enone precursors (Scheme 1). The spontaneous double cyclisation is initiated by the regio- and stereo-selective installation of a chiral amine nucleophile, using a TA enzyme. This methodology represents the first example of an enzyme-triggered DIMAMR, and negates the need for chiral auxiliaries/catalysts, unfavourable reaction conditions, and multi-step synthesis for forming highly complex indolizidine and quinolizidine structures.



Scheme 1: *Biocatalytic routes towards N-heterocycles utilising a TA-triggered double intramolecular aza-Michael reaction (DIMAMR).*

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Biocatalytic Cascades For The Synthesis of Therapeutic Iminosugars From Monosaccharides

Kathryn Yeow, Elaine O'Reilly

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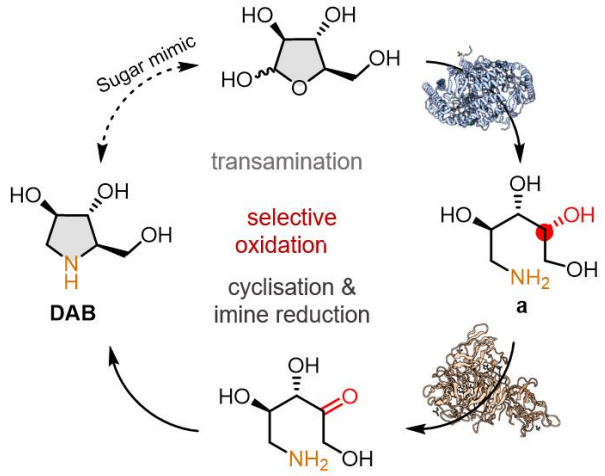
Iminosugars, such as DAB (1), are polyhydroxylated *N*-heterocycles with the nitrogen in place of the sugar ring oxygen. These naturally occurring compounds are monosaccharide mimics with pharmaceutical importance, they interact with and inhibit carbohydrate processing enzymes and possess beneficial drug-like properties. [1] Conventional syntheses of iminosugars from readily available carbohydrates is challenging mainly due to the presence of multiple hydroxyl groups, and relies heavily on protection-deprotection steps to perform regioselective transformations. [2]

Inspired by a proposed biosynthetic pathway for transformation of fructose-6-phosphate into an iminosugar scaffold, [3] we demonstrate a three step chemo-enzymatic synthesis, whereby minimally protected monosaccharides undergo transamination, selective oxidation, and reduction, *via* transaminase, oxidoreductase, and catalytic hydrogenation steps, respectively. [4-6] Furthermore, we develop a one-pot biocatalytic cascade that is fully protecting-group-free, with high conversions from the monosaccharide to the valuable iminosugar compounds without isolation of intermediates.



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Exploring the effect of aging ether-based electrolyte on the cycle life of lithium metal batteries

Abstracts

Keith Sirengo, Barry Brennan, and Suresh Pillai

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Highly reactive lithium anode has the potential to replace conventional graphite electrodes. However, the reaction with organic electrolytes results in constant breaking of the SEI layer, reducing the battery's cycle life. This work reports the stabilization of lithium metal surfaces with organic electrolytes before cycling by aging the cell.

The primary focus was on time-dependent studies where the coin cell was fabricated and pretreated in Lithium bis((trifluoromethyl)sulfonyl) amide 1M LiTFSI /DME/DOL (1:1) for different number of days before cycling. SEM investigated the surface morphology of the lithium surface was smoother for the aged cell than an as-prepared cell. Symmetrical cells showed that 16 days of pretreatment displayed low polarization and longer cycle life.

The pre-pretreated coin cell displayed 80% capacity retention after 50 cycles compared to the untreated cell (20%). This improved performance is probably due to the in-situ spontaneous polymerization of the 1,3 dioxolane, resulting in a flexible SEI layer.

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Effects of Non-thermal Plasma Treatments on Commercial Fabrics for Application in Textile Triboelectric Nanogenerators

R. Walden[1,2,3], B. Soltani [4], B. Brennan[1], Jungmi Hong[4], P. J. Cullen[3,4], and S. C. Pillai[1,2]

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Corresponding author: Ryan Walden (*Ryan.Walden@research.atu.ie*)

Triboelectric Nanogenerators have proven to be an effective method of electrical energy generation and their efficiencies have shown a steady increase [1]. However, the development of textile-based TENG devices (T-TENGs) has been slow and challenging at times. By utilising commercially available materials, the major issues are related to the scale-up of the treatment process, increasing the longevity and electrical efficiency of textile triboelectric materials. By utilizing dielectric barrier discharge (DBD) plasma (Figure 1), it is possible to modify the surface functionality of fabrics. DBD plasma generates free radicals, functional groups and ions that bombard the surface of the materials, removing weak ionic bonded groups and replacing them [2]. Since triboelectricity is primarily the movement of electrons between the surface of opposingly charged materials, this replacement of surface functional groups directly affects the electrical properties.
This study represents a comparative look at plasma treatments from an electrical perspective and a step towards fully wearable T-TENG devices. Detailed investigations are currently underway to understand the mechanism by which plasma gases influence the triboelectric properties of polyester fabrics. After plasma optimisation and treatment these functionalised fabrics are systematically characterised using XPS, FTIR, contact angle and electrical characterisation, to compare the effects of each plasma on the material surface. Electrical changes prove that through basic plasma treatments it is possible to influence the overall electrical outputs of fabric materials and thus the overall efficiency of T-TENGs.

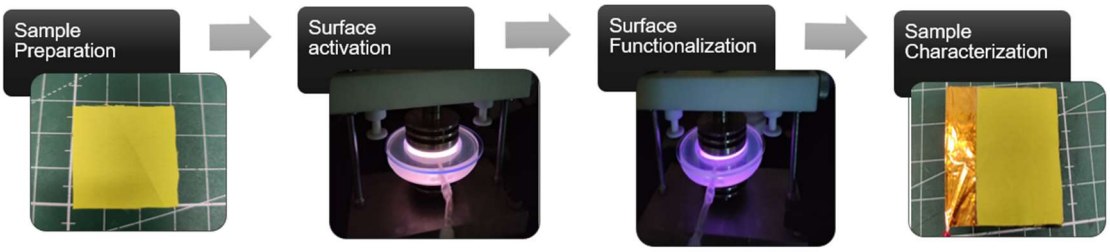

Figure 1:Experimental procedure for plasma treatment of polyester fabric.

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Heterogeneous catalysts for promotion of Artificial Photosynthesis

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Approximately 80% of global energy generation comes from combustion of fossil fuels [1]. However, temperature increases due to rising CO_2 levels are projected to have many negative impacts, and therefore scientists are looking for methods to ameliorate this. One method is the artificial photosynthesis (AP) reaction. Reacting CO_2 with H_2O to form CO or hydrocarbons over a catalyst using a sustainable energy source has become hugely desirable. The success of this process would contribute to the goal of creating a circular carbon economy. AP can be carried out using semiconductor photocatalysts. However, as semiconductors have several limitations (*e.g.* wide bandgaps are needed to reduce electron/hole recombination, but this also reduces the amount of usable sunlight), modifications need to be made.

Several types of catalysts are investigated in this research. The first are Z-scheme systems. These consist of a reduction semiconductor photocatalyst coupled with an oxidation semiconductor photocatalyst. "Z-scheme" is the term used to explain the observed efficient electron/hole separation mechanism obtained using the two co-located semiconductors [2] .The second are plasmonic systems. Certain metals or conducting metal oxides can interact with UV/visible photons to give rise to excitation known as surface plasmon resonance, the oscillation of free electrons on the surface of a particle. These plasmons can decay *via* the generation of catalytically useful "hot electrons" [3].

Each material is fully characterised to probe their electronic, physical, and chemical properties before testing their activity in the AP reaction under batch conditions.

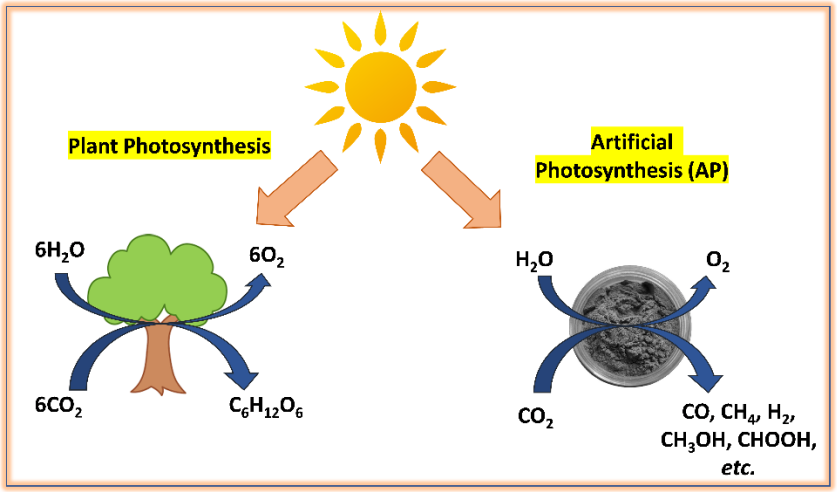

Fig.1: Natural photosynthesis (left) *vs.* artificial photosynthesis (right).

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Carbon-encapsulated metal N-doped porous materials: A promising architecture for electrocatalytic hydrogenation of biomass derivative organics

Filippo Pota[1], Maida Aysla Costa de Oliveira[1], Christian Schröder[1], Marc Brunet Cabré[1], Hugo Nolan[1], James A. Behan[2], Frédéric Barrière[2], Paula E. Colavita[1]

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Nowadays from biomass it is possible to obtain valuable chemicals and fuels using methods that involve precious metal catalysts, high temperatures and pressure.[1] This is seen as a significant approach in mitigating carbon emissions, even if the extreme conditions and the use of catalysts based on expensive metals raises concerns about the sustainability of the strategy. Electrocatalytic hydrogenation (ECH) offers an eco-friendly alternative by utilizing in situ generated hydrogen to catalyze the conversion of organic molecules from biomass, and at the same time eliminate the necessity for high-purity hydrogen and high pressures. Notably, literature underscores the potential of precious metals and carbon-supported precious metal (M/C) as promising electrocatalysts for ECH.[2]

In this work we focused on the design, synthesis and characterization of heteroatom doped carbon-based materials with base/abundant metal incorporation and explored their potential as electrocatalysts, particularly in ECH. A versatile hydrothermal method was employed to introduce different metallic nanoparticles and heteroatom functionalities into a nanocarbon scaffold with high conductivity and porosity. Electrochemical characterization involved voltammetry and chronoamperometry on different conductive carbon supports using benzaldehyde as a diagnostic substrate. Chromatographic product detection coupled to electrolysis experiments facilitated the determination of efficiency and selectivity in organic hydrogenations. The results provide insights into reactivity trends based on the choice of metal core, metal loading, and the potential for achieving selectivity in organic transformations relevant to sustainability. Moreover, measurements of turnover frequencies (TOF) enabled a comparison of the performance of prepared materials against that of precious metals supported on carbon, with encouraging results.[3]

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Ceramic fillers incorporated Polyvinylidene Fluoride (PVDF) and Nylon-6 Polymer nanocomposites for Self-powered Triboelectric Nanogenerators (TENGs)

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In recent research, polymer composites have emerged as promising materials in utilising triboelectric nanogenerators (TENG), considered efficient technology for harvesting mechanical energy. In this work, we have demonstrated, for the first time, the role of different crystalline phases of TiO_2 and Cobal Aluminum layered double hydroxide (CoAlLDH) in enhancing the TENG performance of PVDF and Montmorillonite (MMT) clay ceramic fillers in enhancing the TENG performance of Nylon-6. The electrical studies of both PVDF/TiO_2 and PVDF/CoAlLDH composites TENGs showed considerable enhancement in the TENG performance of the polymers by compositing them with the fillers. In the case of PVDF/TiO_2 TENG, rutile phase TiO_2 ($rTiO_2$) was found to enhance the TENG performance of PVDF by 50% compared to that of the anatase phase of TiO_2. PVDF-$rTiO_2$ composite produced a voltage of 60V and 3 µA current under a frequency of 8Hz at 60N force. Whereas the PVDF/CoAlLDH TENG showed a voltage output of 95V and 6 µA current under a frequency of 10Hz at 20N force. TENG performance of Nylon-6 was also enhanced 4 times by incorporating exfoliated and unexfoliated MMT fillers. Additionally, the voltage output of all the TENG devices was observed to be stable throughout a continuous 16000 cycles (2000s) of oscillation. XRD, FT-IR, XPS, analysis of the fillers and SEM, and 3-D profilometry of polymer composites validated the materials' structural and compositional aspects which explain the enhancement of the TENG performance of these polymers by compositing them with ceramic fillers like TiO_2, CoAlLDH and MMT. The energy harvesting and storage abilities of the developed TENGs were demonstrated by lighting up 56 LEDs and charging capacitors ranging from 1 µF to 50 µF using the output from the devices. These demonstrations show the self-powering ability of the developed TENG.

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Towards Sustainable Nanomaterials: Greener Routes to Quantum and Carbon Dots

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Quantum dots are nanomaterials so small that their size determines their properties.[1] Last year the Nobel Prize in Chemistry was awarded to Moungi G. Bawendi, Louis E. Brus and Aleksey Yekimov for the discovery and synthesis of quantum dots.[2-4] Now they spread their light from televisions and LED lamps and guide surgeons when they remove tumour tissue, among many other things. As their technological and industrial importance grows, so too does their demand and prevalence; however conventional quantum dots are based on toxic heavy metals with potentially significant health impacts, and which carry a high environmental burden in both extraction and disposal.

In recent years carbon dots, nanoparticles of graphitic or polymeric carbon, have emerged as a cleaner, greener, non-toxic alternative, with proven potential in many of the same applications, with the added benefit of biocompatibility for biomedical uses.[5] Importantly carbon dots may be prepared by environmentally benign hydrothermal treatment of almost any carbon source including biomass.[6] This offers a route to in-demand, eco-friendly, functional nanomaterials by the treatment of waste streams or upgrading of biomass, creating opportunities for significant added value across multiple sectors.

Here, we report on our recent efforts towards developing greener routes to conventional quantum dots, minimising the environmental and societal impacts of this important class of materials. We further discuss the production of carbon dots from locally sourced seaweed feedstocks, bypassing many of the concerns associated with conventional quantum dots.

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AN ELECTROCHEMICAL OXIDATION PRINS-TYPE CYCLISATION SEQUENCE FOR THE CONSTRUCTION OF 1,3-OXAZINAN-2-ONES *VIA N*-ACYLIMINIUM IONS

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Nitrogen-containing heterocycles represent one of the privileged structural motifs in synthetic pharmaceuticals and are also widely found in naturally occurring compounds. [1] Among various synthetic strategies for the functionalization of nitrogen-containing compounds, the electrochemical oxidation (also known as Shono oxidation) [2,3] has gained increasing popularity as a powerful and green strategy to selectively and efficiently oxidise a C-H bond in the *α* position to the nitrogen atom.

In this project (**Figure 1**), we perform the electrochemical oxidation using an ElectraSyn device, and then use a Prins-type cyclisation to construct the 1,3-oxazinan-2-one skeleton **(4)** from a variety of cyclic and acyclic *N*-Boc compounds **(1)**. The scope of the sequence to date and its stereochemical outcome will be described, which includes the substituents (R), ring size and acyclic examples. Also included will be the optimisation of the Prins-type cyclisation to form **(4)**.

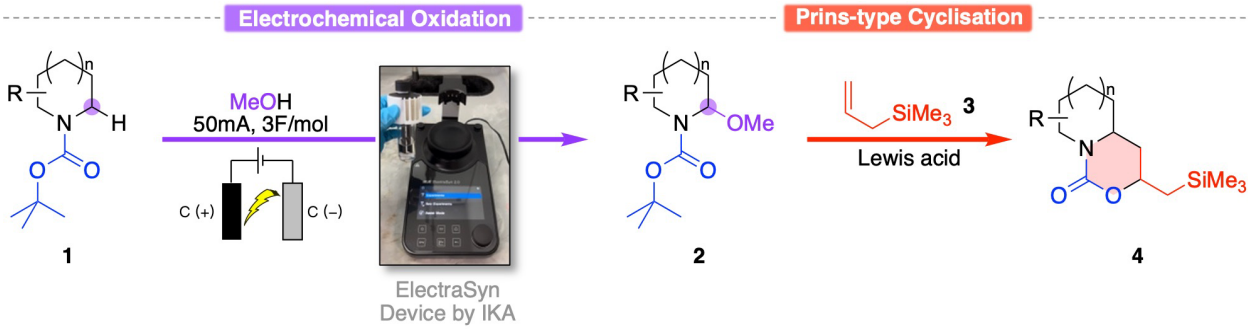

Figure 1. An Electrochemical Oxidation Prins-type Cyclisation Sequence

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The Integration of Continuous Flow Technology with Strained Cyclic Systems

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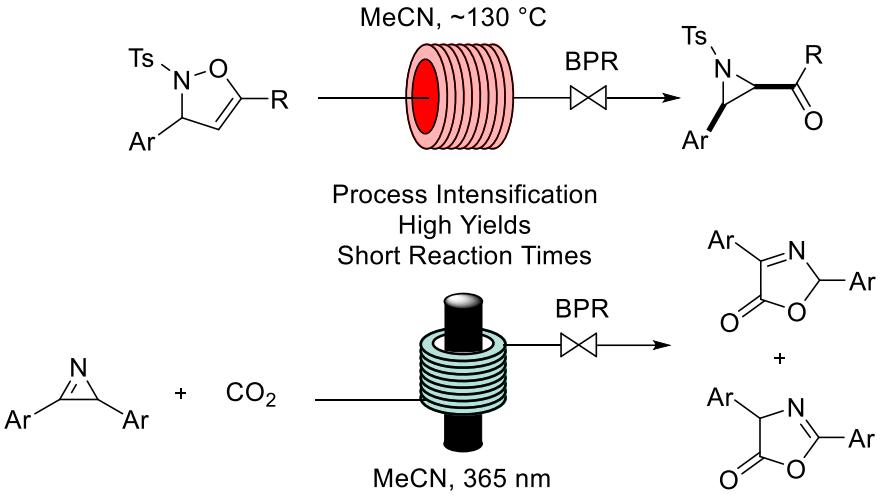
Modern chemical synthesis relies on traditional batch synthesis or technology. As technology has developed, chemists have started to incorporate new enabling technologies to improve synthetic methodologies. One such enabling technology is continuous flow chemistry. Several works in the literature have demonstrated that performing chemical reactions in continuous mode, using tubing as vessels, lead to a number of advantages; for example, improved heat and mass transfer, safety, and scalability, are exploited to improve chemical processes and often, perform chemical reactions that have been forgotten or are forbidden in batch. [1] This talk focuses on the integration of continuous flow technology with strained cyclic systems, namely aziridines and 2*H*-azirines.



Acylaziridines were synthesised *via* a thermal Baldwin rearrangement process. Discovered in the 1960s, this thermal ring contraction of isoxazolines into valuable aziridine molecules was greatly improved upon its transfer to continuous flow, which achieved higher yields and throughputs, shorter reactions times, and a broader substrate scope than the corresponding batch procedure. [2] 2*H*-Azirines are highly reactive molecules and serve as useful precursors in photochemical cycloaddition reactions. [3] The uniform irradiation and short path lengths associated with photochemical flow processes were exploited in the irradiation of 2*H*-azirines, resulting in ring opening of the azirine and subsequent cycloaddition with CO_2, yielding the oxazolone products in less than a 15 minute residence time. Current work focuses on expanding the library of oxazolone products.

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The Development of Novel Ferrocenyl Compounds *via* Acid-Mediated Transformations and the Diastereoselective Synthesis of a Novel Tricyclic Indene

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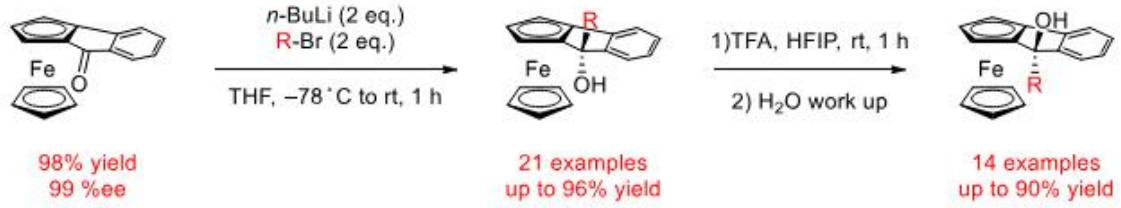
Ferrocene was discovered in 1951 by Kealy and Pauson and has since found uses in asymmetric catalysis, organometallic chemistry, and medicinal chemistry.[1] The Guiry group have previously reported the optimised synthesis of chiral ferrocenyl scaffolds and applied these as ligands in asymmetric catalysis.[2] This project investigates acid-mediated transformations of ferrocenyl alcohols. The reactivity and selectivity of the ferrocenyl monoketone has been exploited in this project for the synthesis of 22 chiral α-ferrocenyl alcohols in high yields of up to 96%. The acid-mediated inversion of the chiral centre at the α-ferrocenyl position was reported in 2020.[3] The scope of this reaction has been further investigated in this project to access 14 inverted chiral alcohols in high yields of up to 90%. Potential uses of the inverted ferrocenyl alcohols are currently under investigation.

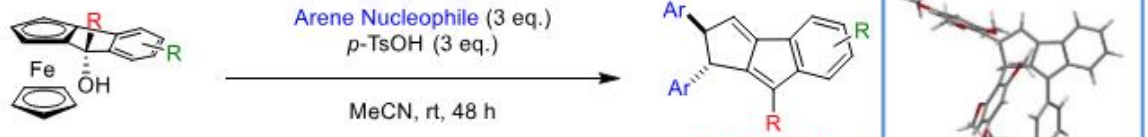


98% yield
99 %ee

21 examples
up to 96% yield

14 examples
up to 90% yield

A novel tricyclic indene has been synthesised *via* an acid-mediated arylation of ferrocenyl alcohols. An unprecedented di-C-H-functionalisation of the unactivated cyclopentadienyl ring of the ferrocenyl alcohol results in deprotection of the fulvene and a loss of iron. This is a diastereoselective reaction as only the *trans*-tricyclic indene is observed, and *cis*-addition does not occur. The mono-arylated side product has been identified by HRMS and a reaction mechanism has been proposed. The structure of the tricyclic indene has been confirmed by X-ray crystallography. The scope of this reaction includes 14 examples isolated in up to 52% yield and 68 %ee.



14 examples
up to 52% yield
up to 68 %ee

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STEREOSELECTIVE SYNTHESIS OF α-GLYCOSIDES

O16

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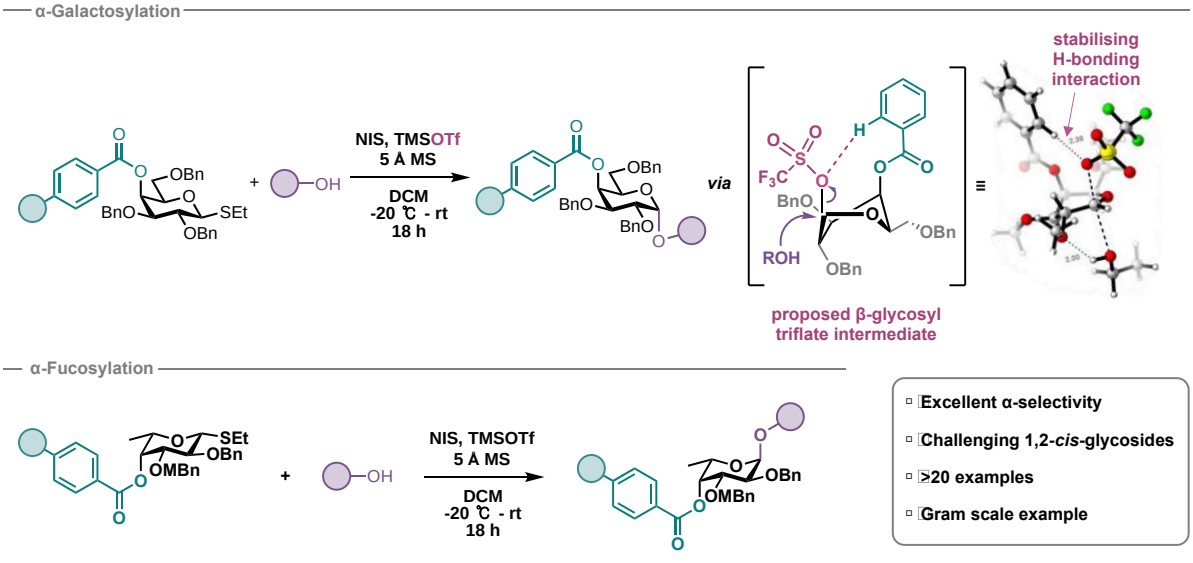
This work is concerned with stereochemical control in α-galactosylation and α-fucosylation reactions. α-Galactosyl and α-fucosyl motifs are prevalent in many biologically important compounds, for example in cancer-associated mucin-type glycans.[1] However, existing methods for their α-selective synthesis that are broadly applicable to a range of substrates are limited.[2-5] Thus, further understanding around the stereochemistry of α-galactosylations and α-fucosylations is required.

This presentation will describe a highly α-selective methodology for galactosylation and fucosylation that employs an orthogonal *para*-substituted benzoate protecting group at position four of the donor substrate. Notably, donors bearing *para*-electron-withdrawing substituents afforded the highest α-selectivities. This is contradictory to existing mechanistic proposals described in the literature that suggest reaction *via* a dioxolenium cation intermediate. Computational and experimental investigations have enabled the development of a new proposal involving H-Bonding to rationalise the excellent α-stereoselectivity in galactosylation described.

The scope of glycosylation has been expanded to accommodate galactosyl- and fucosyl-α-1,3-, α-1,4-, and α-1,6-linkages with exclusive α-selectivities, including a gram-scale example. The application of this glycosylation methodology to the synthesis of target compounds will also be described.[6]



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IRISH RESEARCH COUNCIL
An Chomhairle um Thaighde in Éirinn

Laccase Oxidation Studies

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Throughout the past four years, the PhD project was focused on developing novel Laccase-mediator reactions[1] and their application, more specifically the Laccase/TEMPO system. The work can be divided into 6 work packages:

WP1: Benzyl alcohol oxidation using the Laccase/TEMPO system.
WP2: Selective N-debenzylation of aryl-halogenated amines using the Laccase/TEMPO system.
WP3: Utilizing the 'microbubble' equipment for improving Laccase/TEMPO benzyl alcohol oxidation.
WP4: Telescoping benzyl alcohol oxidation into the Kabachnik-Fields reaction.
WP5: Screening of Almac's in-house 96 Laccase enzymes on benzyl alcohol oxidation.
WP6: Discovering novel Laccase/TEMPO oxidation reactions.

The focus of this presentation will be on WP2 and WP4.

The benzyl group is a common protecting group for amines.[2] Conventional N-debenzylation is performed via hydrogenolysis using H_2, Pd/C, however it causes inevitable cleavage of aryl-halogen bonds limiting the design of synthetic routes. Oxidative N-debenzylation using the Laccase/TEMPO system has been reported before[3], however it has yet to be explored with halogenated substrates. Based on our previous experience with halogenated benzyl alcohols, our work studied the use of Laccase/TEMPO system as a selective, greener, and robust alternative to conventional methods for N-debenzylation that avoided dehalogenation, using a range of aryl-halogenated amines substrates.

The Kabachnik-Fields reaction is a three-component reaction between aldehyde, amines, and phosphite to synthesize α-aminophosphonates[4], a bioisostere of α-amino acids. This work studied the telescoping of benzyl alcohol oxidation using the Laccase/TEMPO system with the Kabachnik-Fields reaction using aqueous buffer in a one-pot two-step approach via micellar chemistry using SDS.

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Superhydrophobic candle soot based anti-icing coatings through environmentally friendly synthesis methods

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Hydrophobic and superhydrophobic surfaces are of interest in many energy and environmental applications [1]. Nevertheless, the strategies to develop such materials often require complex pathways and the use of toxic solvents or fluorine containing materials. Previously, several researchers proposed using low toxicity candle soot to achieve superhydrophobic properties but in most cases the soot particles showed poor mechanical stability. In some studies, to enhance the stability, soot particles were incorporated in a binding matrix. However, toxic solvents such as hexane or chloroform have been frequently used [2,3]. Moreover, the hydrophobic properties in all such cases are due to the materials utilized as binder matrices. The use of SiO_2 as a top binding layer using TEOS vapor deposition has been utilized by researchers however the hydrophobic nature of soot particles cannot be exploited in such cases due to the inherently hydrophilic nature of SiO_2. To overcome such challenges, we synthesized candle soot-based superhydrophobic coatings on glass and copper substrates. A layer of candle soot was first deposited on the surface and subsequently infused with TEOS. The conversion of the infused TEOS to silica-based binder matrix is achieved by a thermal combustion route. Due to the self-assembly of soot particles in the top layer, the surfaces maintain their superhydrophobicity without any additional treatment. FESEM, optical profilometer and EDX based quantitative and qualitative measurements then assessed the morphology, surface roughness parameters and composition respectively. The droplet dynamics were recorded for a 10 µl droplet falling from a 10 cm height and the changes in droplet shape were discussed with respect to the roughness scale. Water droplet and jet impingement tests showed enhanced stability of the soot particles on copper and glass substrates. These surfaces were further infused with PDMS oil (50 cSt), resulting in slippery lubricant infused porous surfaces (SLIPS). Self-cleaning studies show highly mobile water droplets carrying off the surface contamination on both the superhydrophobic and SLIPS surfaces. Centrifugal ice adhesion tests conducted over the soot-TEOS deposited copper surfaces were positive and showed ultra-low ice adhesion (<20 kPa) in repeated trials. We expect the reduced usage of toxic chemicals will provide greener synthesis protocols and better prospects for large-scale synthesis of ultra-low adhesion icing resistant coatings.

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Electro-guided Soft Micro-vehicles: From Polymer Microstructures to Ionic Liquid Droplets

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Electro-responsive soft materials hold great appeal for the realisation of micro-vehicles due to their ability to translate an electrical stimulus into a mechanical response, thereby achieving programmable and autonomous motion of matter.[1]

In this work we demonstrate two types of materials suitable for the development of electro-guided micro-vehicles: 1) electro-active hydrogels (EAH), and 2) electrotactic ionic liquid (IL) droplets. In both cases, their electro-actuation is driven by a redistribution of mobile ions within their system.

In the case of EAH, asymmetric distribution of ions creates an osmotic pressure gradient ($\nabla\pi$), leading to the directed diffusion of water within the hydrogel network, driving its unidirectional actuation (*e.g.* bending).[2] To date, actuation times reported for EAH are long, typically in the order of minutes and even hours, due to the dimension-dependent kinetics governing the diffusion process. Herein, we demonstrate for the first time, fast actuation in EAH, with sub-second response times, by fabricating EAH microstructures *via* two-photon polymerisation (2PP). Their electro-actuation was optimised by varying the aspect ratio of the microstructures along with experimental conditions such as pH and concentration of the electrolyte, and the electric field strength and direction. We showcase the advantages brought by combining 2PP with EAH, through the fabrication of micro-electro-actuators of complex design, to produce fast and programmable 4D actuation.

In the case of electrotactic droplets, asymmetric distribution of ions creates a surface tension gradient ($\nabla\gamma$), leading to the generation of Marangoni flows inside and outside the droplet, driving its electro-activated propulsion (*i.e.* electrotaxis).[3] Droplet taxis was characterised as a function of the ionic strength and surface tension of the surrounding electrolyte solution, and the strength and direction of the applied electric field. Upon system optimisation, reversible droplet electrotaxis with speeds up to 0.71 ± 0.13 body length·s^{-1} was achieved. Furthermore, we demonstrate that such electrotactic droplets can be employed as micro-vessels for cargo transport and release, and for sensing and reporting on their local chemical environment.

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Zeolite EMT Entrapped Ruthenium Polypyridine Materials for Photocatalytic Degradation of Pollutants

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The prevalence of organic contaminants in wastewater is a major concern. These compounds have an adverse effect on marine life as well as humans, and it is therefore imperative that an environmentally harmonious solution is found to mitigate this problem. Photocatalysis offers the opportunity to utilise photoactive molecules and visible light to effect cheap and efficient degradation of hazardous pollutants.[1] The intracrystalline void space within zeolites provide a versatile host environment for the inclusion of photoactive molecules to act as heterogenous photocatalysts. The advantage of these systems includes high chemical stability and ease of recovery.

The inner cages of zeolite EMT are large enough to accommodate ruthenium polypyridyl complexes which function as the photosensitiser molecules. Encapsulation of the photoactive guest is achieved through the ship-in-a-bottle synthesis method, whereby small reagents diffuse through pore openings into the zeolite cavities, then forming the final product. Due to their large size and molecular restrictions placed on them by the zeolite cages, once formed, these molecules are permanently immobilised.[2]

Once synthesised, the spectroscopic properties of these materials were assessed using a variety of characterisation techniques. Changes to the emission and vibrational spectra of the photosensitiser molecule were observed, caused by the space constraints of the zeolite matrix.[3] Catalytic performance of the materials was assessed using a photoreactor setup. Preliminary results show encapsulated ruthenium tris-bipyridine and tris-phenanthroline materials were able to degrade methylene blue dye under visible light irradiation. A library of photoactive materials can then be created in the future, along with assessment of their photocatalytic performance.

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NANOCOMPOSITE PHOTORESISTS FOR STRUCTURAL COLORATION

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The interaction of light with micro- or nanostructures present in natural organisms often results in a vibrant and dynamic type of colour known as structural coloration. Fascinating examples of structural coloration in animals include the brilliant iridescent wings of the *Morpho* butterfly resulting from thin film reflectance, opals in beetles due to photonic crystals and the lustrous surface of the mollusc *Haliotis Glabra* caused by diffraction gratings.[1] On the macroscale, its resistance to fading and tunability of colour have resulted in manifold applications. On the microscale, its exploitation in chemical sensing, data encryption, and optical devices holds enormous untapped potential.

Herein, we present a novel strategy to creating photonic microstructures using direct laser writing (DLW) via two photon polymerisation (TPP). DLW-TPP is a maskless optical lithographic technique that enables fabrication of complex 3D microstructures with sub 300 nm resolution and minimal topological constraints.[2] This work demonstrates development of two different types of novel nanocomposite photoresists suitable for DLW-TPP for the fabrication of responsive photonic microstructures.

In the first example, silica particles (SiO_2 NPs) were incorporated into compatible acrylate-based photoresists at varying concentrations, to form highly stable dispersions. Photopolymerisation of these nanocomposite photoresists via DLW-2PP allowed for the realisation of photonic microstructures responsive to changes in immersion solvent, yielding a wide gamut of tuneable colours covering the entire red–green–blue (RGB) colour space. Furthermore, the presence of SiO_2 NPs endowed significant mechanical reinforcement properties to the microstructures, which was confirmed via AFM and scanning electron microscopy (SEM).[3] The second nanofiller investigated was cellulose nanocrystals (CNCs). At relevant concentrations, CNCs have the ability to self-assemble into a left-handed chiral nematic (cholesteric) phase. This was demonstrated in selected photoresists allowing for tunability of the reflected colour depending on the pitch of the cholesteric phase. Vibrant colours over a wide range of the visible spectrum were yielded and these colours were dynamically changed in response to the local chemical environment. Such photonic microstructures find application in colour displays and encryption micro-devices.

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Direct Laser Writing of Complex 3D Metal Nanoparticle Patterns within Polymer Microstructures for Photothermal Micro-Actuators

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This work describes the fabrication of complex 3D structures comprising of metallic Ag nanoparticles (NPs), manufactured within prefabricated polymer structures by direct laser writing (DLW). In recent years, DLW has been established as a micro-fabrication technology to produce 3D micro-objects with features below 300 nm. This additive manufacturing technology is an adaptable, high-resolution process, where structure fabrication can be achieved via multi-photon polymerisation or metal ion photo-reduction.[1] More recently, this technique has been applied to the fabrication of stimuli-responsive hydrogel microstructures. In this context, stimuli-controlled hydrogel micro-actuators show improved performance compared to their macro-scale counterparts due to their augmented surface to volume ratio, and find applications across many fields including micro-robotics, microfluidics and biomedical devices.[2]

The microstructures described herein were realised using a two-step approach. The first step comprised the fabrication of polymer structures via DLW by free-radical polymerisation. Following their fabrication, the polymer structures were immersed in a solution of Ag^+ and a second DLW process was conducted to induce photoreduction of the Ag^+ ions, thereby creating complex patterns of Ag NPs inside the 3D polymer microstructures. TEM and SEM characterisation of microstructure cross-section was used to characterise the metal particle size and NP distribution.

The same two-step approach was used to create microstructures showing photo-induced actuation. In this case, the microstructures were fabricated in the thermo-responsive polymer poly(*N*-isopropylacrylamide) (pNIPAAM). pNIPAAM has been extensively employed for the realisation of thermo-actuators, owed to its thermo-responsive properties associated with a phase transition at the lower critical solution temperature (32 ˚C).[3] Ag NP patterns were then written *in situ* inside the pNIPAAM microstructure, to act as photothermal converters. Laser irradiation of the Ag NPs patterns caused localised heating, inducing fast, controllable and reversible actuation of the microstructures. We further demonstrate how the actuation direction and speed can be tuned via the design of the Ag NP pattern or the laser parameters such as scan speed.

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Antibacterial Polymers Mimicking Antimicrobial Peptides

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Abstract

Antimicrobial peptides (AMPs) are of pharmaceutical interest due to their ability to kill microbes while also proving difficult for microbes to develop resistance against. Due to the ever-increasing emergence of microbes that are resistant to common antibiotics, coupled with the lack of new antibiotics being developed, research in the use of AMPs as therapeutics has been investigated[1]. For a peptide to have an antimicrobial effect, it typically has to contain hydrophobic and cationic amino acid residues. This allows the peptide to interact with anionic lipids and insert into the microbial membrane and disrupt it by creating pores, resulting in cell death through lysis. This membrane-targeting is what makes antimicrobial peptides difficult to evolve resistance against. However, problems with AMPs arise from their stability due to their polyamide backbone, which is susceptible to protease degradation thereby decreasing the peptides' bioavailability[2].

This research aims to develop AMP mimetics which possess a polyethylene glycol (PEG) backbone in place of the natural polyamide chain, while also retaining hydrophobic and cationic side-chains similar to amino acids. Related candidates based on a poly(glycerol) backbone are also investigated as part of these studies. Different cationic and amphipathic co-polymers have been prepared, characterized and evaluated for their antibacterial activities against representative Gram-negative and Gram-positive organisms (*E. coli* and *S. aureus*). They consistently contain guanyl units as cationic content, while variable hydrophobic units functionalized with branched or aromatic side-chains were used to optimize the MICs of these peptidomimetics, providing candidates with activities similar to the parent AMPs.

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Discovery of small molecules blocking a key binding site in SARS-CoV-2 nsp3 protein

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Abstract:

As new medications are used to treat COVID-19, many studies have reported that proteins such as spike, polymerase and proteases are prone to high levels of mutation that can create resistance to therapy over time [1]. Thus, it becomes necessary to, not only target other viral proteins such as the non-structural proteins (nsp's), but to also target the most conserved residues of these proteins.

A synergistic combination of bioinformatics, computer-aided drug-design and *in-vitro* studies can feed into better understanding of SARS-CoV-2 (SC-2) and therefore help in the development of small molecule inhibitors against the nsp's [2]. As part of our initial anti-viral work, a pharmacophore study on nsp15 found a hit molecule (INS316) that made interactions with Ser293, Lys344 and Leu345 residues [3] which are highly conserved across SC-2.

We have performed multiple sequence alignment studies on different datasets i.e., ~200,000, ~1 million and ~11 million sequences of SC-2 Orf1ab sequences to identify the most conserved residues. These residues were then visualized on 3D protein X-ray structures using MOE software. We found that there were known and novel binding pocket residues that were 100% conserved in our datasets. Our results indicate that these highly conserved pockets can be targeted for developing promising SC-2 inhibitors. We have also performed mutational analysis and have found different mutational hotspots across the nsp's.

Our group was selected to enter an international challenge organized by CACHE to find inhibitors for the Mac1 domain of SC-2 nsp3. We used a tiered screening workflow which included the use of volume/shape information of the binding pockets (fastROCS), use of in-house pharmacophore generation software (MoPBS [4]/MOE) and performed docking in the binding pocket (FRED) to rank compounds for subsequent clustering and to identify hits that bind to these conserved pockets. The primary experimental validation results provided by CACHE have identified two of our predicted hits that shows activity in HTRF and SPR assays.

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Design and synthesis of novel antimicrobial peptides replacing amino acids with conventional small molecule antibiotics producing an amalgamation of a peptide mimetic/conjugate system

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Antimicrobial resistance has become a global challenge associated with nearly five million deaths in 2019.[1,2] Antimicrobial peptides (AMPs) have innate advantages to overcome resistance including electrostatic-driven selectivity towards microbial membranes, broad spectrum of activity and generally a non-specific membranolytic-based mechanism of action.[3] However, AMPs have little predictability in sequence and length thus researchers generally rely on natural peptide scaffolds, intuition or computational design to produce active amphiphilic structures which characterise AMPs. Several groups have shown AMP containing non-canonical amino acids[4–7] can be active; however these are generally used for fluorescent labelling or circumventing proteases. Our research involves using fluoroquinolones (FQs) as tryptophan surrogates to amalgamate the advantages of AMPs and conventional antibiotics, producing hybrids of peptide mimetics and conjugates. Replacement of tryptophan residues in AMPs with FQs, particularly ciprofloxacin, has produced a series of candidates which have shown good antimicrobial activity, particularly against Gram-Negative bacteria such as *E. coli* and *P. aeruginosa* with minimum inhibitory concentrations of <10 µM. Additionally, antibacterial assays with FQ resistant bacteria have suggested the FQ moiety remains active even within a peptide chain. It is hoped these hybrids of peptide mimetics and conjugates will help explore the role of tryptophan in AMPs as well as being useful in the design of AMP therapeutic candidates with improved pharmacokinetic properties.

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Antibiotic Metabolites: Synthesis, Characterisation, and Assessment of their Role in Antibiotic Resistance Development

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Bacterial antimicrobial resistance (AMR), a global public health crisis, was associated with an estimated 4.95 million deaths in 2019.[1] Antibiotic resistance emerges when bacteria acquire the ability to withstand antibiotic treatment.[2] Antibiotic metabolism by liver enzymes in humans and animals results in the generation of antibiotic metabolites post-treatment. These metabolites often have structural similarities to their parent antibiotics and, in some cases, exhibit antibacterial properties themselves. Antibiotics and their metabolites can be found in wastewater treatment plants, agricultural runoff, and hospital effluent, ultimately infiltrating our environment.[3] Exposure to sub-inhibitory concentrations of antibiotics can promote the development of bacterial resistance, yet the extent to which bacterial exposure to sub-inhibitory levels of metabolites contributes to resistance against parent compounds remains unknown.[4]

We have adapted and improved existing literature methods for the synthesis of several of the main human metabolites of commonly prescribed antibiotics from three different antibiotic classes, namely Ciprofloxacin, Amoxicillin, and Sulfamethoxazole; antibiotics which have been detected in the environment previously.[5] Notably, we employed microwave assisted synthesis (MAS) to obtain two of the ciprofloxacin metabolites, which has not been reported previously. We have synthesised the metabolites in quantities sufficient for a wide range of microbiological studies. To date, we have conducted sub-inhibitory concentration studies with two metabolites of ciprofloxacin using the clinically relevant ESKAPE pathogens *Pseudomonas aeruginosa* and *Staphylococcus aureus*; these results will be presented.

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Novel Proton Shuttling Mechanism in Pd(II)-Catalyzed Wacker-type Oxidation

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Wacker oxidations are essential for directly synthesis of carbonyl compounds from alkenes. Although the reaction mechanisms under aerobic conditions are well-understood, their dynamics with peroxides as oxidants remain less explored. Previously, Muldoon and co-workers reported experimental studies on this topic and surprisingly detected a palladium enolate intermediate, indicating an alternative reaction path to the textbook 1,2-hydride shift mechanism [1]. This was also supported by D-labelling experiments conducted by the same authors. However, the steps leading to the formation of this key Pd-enolate intermediate remain hidden, which we have computationally investigated in-depth, uncovering a new dominating proton shuttle reaction pathway [2]. In this oral communication, I will present our comprehensive study of the Wacker oxidation process applied to styrene, utilizing hydrogen peroxide (H_2O_2) and tert-butyl hydroperoxide (TBHP) as oxidants (Figure 1). Through the integration of density functional theory and microkinetic modeling, our findings with H_2O_2 reveal a novel reaction path featuring an intermolecular proton transfer facilitated by the [OTf]− counterion in the medium. I also will show that substituting H_2O_2 with TBHP as the oxidant alters the reaction to favour an intramolecular protonation through the in situ produced HOtBu group. The results explain the observed levels of deuterium incorporation in the final product from experiments using α-d-styrene and D_2O_2. These new mechanistic insights hold promise for directing the synthesis of more effective catalysts for the production of both industrial and fine chemical precursors.

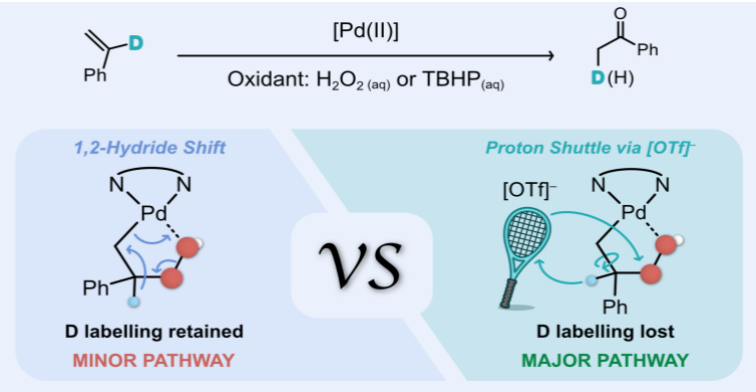

Figure 1. General overview of the 1,2-hydride shift mechanism vs the proton shuttle pathways.

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Mechanistic Insight into Alkali-Metal Mediation of Styrene Transfer Hydrogenation: A DFT Study

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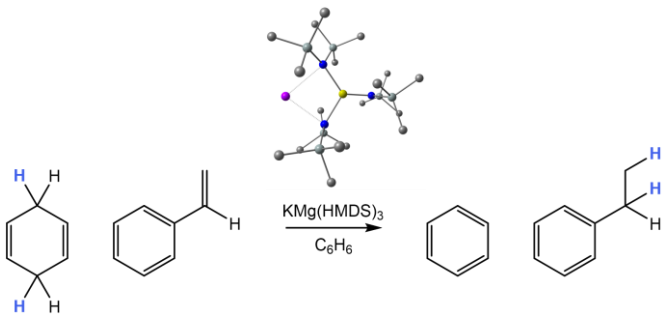
The catalytic hydrogenation of unsaturated bonds is a fundamental reaction in the Chemist's toolbox. It is well known that traditional catalyst systems are based on late transition metals, commonly using molecular hydrogen as the reducing agent. With the awareness of the growing scarcity of heavier transition metals, there have been significant efforts into developing Main Group alternatives. Considering their low toxicity and relative abundance, complexes of group 1 and 2 have become targets as potential mediators in such chemical transformations. Specifically, examples of bimetallic cooperativity have emerged, in which an alkali metal enhances the catalytic ability of another metal such as magnesium or calcium.[1,2] This cooperativity can manifest as: enhancement of nucleophilicity or Lewis acidity, activation of the substrate or even as an anchor point. In light of this, a computational mechanistic study has been performed to investigate the transfer hydrogenation of styrene, catalysed by a potassium tris-hexamethyldisilazide magnesiate, using 1,4-cyclohexadiene as the hydrogen source (Scheme 1). This study, in collaboration with the Mulvey and Robertson groups, follows up a previous systematic exploration of this reactivity.[3] These calculations support this previous work and demonstrate the synergistic effects present in the bimetallic complex. Furthermore, they shed light on the lack of reactivity, or the lack of selectivity observed for the individual monometallic components. Several distinct mechanistic pathways have been explored and will be discussed in this presentation. Further work is ongoing to investigate how the variation of the alkali or alkaline earth metal affects the mode of action of these complexes.



Scheme 1: Transfer hydrogenation of styrene using 1,4-cyclohexadiene as the hydrogen source, catalysed by $KMg(HMDS)_3$.

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A Python-Based Workflow for the Automated Generation of Molecular Libraries

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Recent progress in data-driven methods, such as machine learning (ML) and artificial intelligence (AI), has significantly impelled the discovery of new materials by leveraging large datasets of chemical systems for training and evaluation.[1] The diverse chemical properties and features included in these chemical libraries have allowed researchers to explore the vast chemical space they represent. Databases such as the Materials Project,[2] primarily contain heterogeneous, bulk and surface systems while libraries of inorganic molecules remain less common. The Cambridge Structural Database (CSD),[3] being one such library, comprises a vast array (*ca.* 1.25 million) of unique structures from X-ray and neutron diffraction analyses. Many of these structures constitute transition metal complexes (TMCs). Unlike the Materials Project, the CSD does not include electronic or thermodynamic properties, limiting its use in data-driven applications. Therefore, we believe there is a need to develop accessible and comprehensive databases to facilitate the rapid discovery of TMCs for a variety of applications. To this end, we present a modular workflow to enable the generation of bottom-up molecular databases from a library of *ca.* 41,000 unique ligands derived from the CSD (Figure 1.).[4] The workflow includes a method for assigning formal charges to ligands and incorporates a set of filters enabling users to select ligands that express properties of interest. For example, atomic composition, charge, and coordinating atom types. From the database of 41,000 ligands, the program can combinatorically construct on the order of 1×10^{11} unique TMCs in a variety of octahedral and square-planar geometries. In addition to the default geometries, new geometries can easily be added.

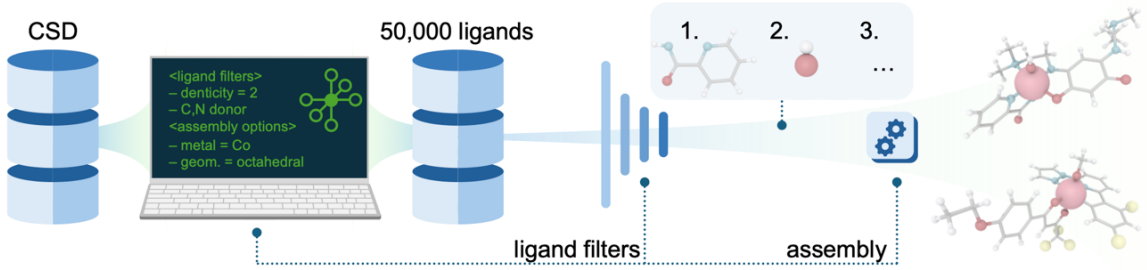

Figure 1. Schematic of the workflow for the generation of TMCs from ligands extracted from the CSD.

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Multifunctional Luminescent Silica Nanoparticles for Applications as Biological Probes and Delivery Agents

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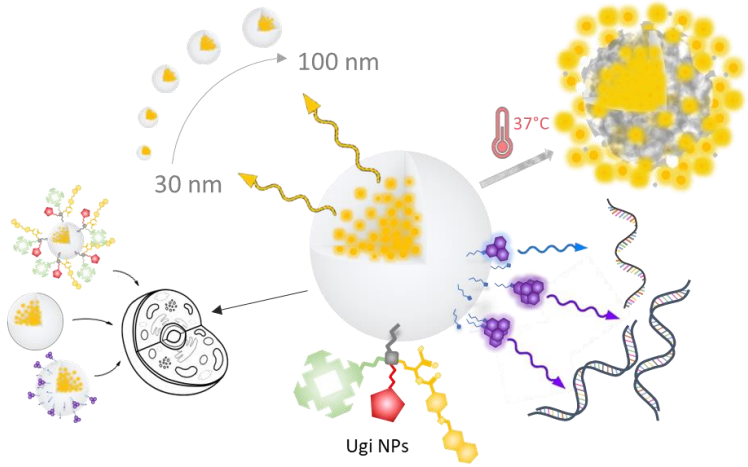
The properties of nanomaterials including controllable size, morphology, surface functionality and biostability make them attractive for biological applications, from drug delivery to biosensing to cellular imaging. Silica nanoparticles (SiO2 NPs) present an ideal candidate for such applications due to their facile synthesis, encapsulation with target molecules, controlled stability and their bioavailability[1,2]. SiO2 NPs smaller than 100 nm are optimally scaled for controlling parameters such as cellular interactions, biocompatibility and controllable dissolution[3].

In this work, the encapsulation of a luminescent species into Stöber type SiO2 NPs of varying size, conveys optical properties to the nanoparticles and establishes trackable materials for sensing applications. Functionalization of the SiO2 NPs surface offers further control of their cellular interactions and stability, while establishing anchors for subsequent modifications. Therefore, these SiO2 NPs can function as delivery systems via enhancements to their dissolution susceptibility, triggering release of the internalized species[4]. The time and temperature dependent dissolution of these emissive SiO2 NPs has been tracked via electron microscopy and spectroscopy.



Scheme 1. Range of properties produced by modifications to NP surface and core

The subsequent modifications to the NP surface with luminescent DNA probes produce multi-emissive, DNA-binding systems with the capacity for multiple sensing events and trackability in cells. Advanced modifications to the emissive SiO2 NPs, via the Ugi multicomponent reaction, give access to multifunctional materials with properties including enhanced cellular recognition and uptake, increased colloidal stability, sub-cellular sensing, and selective binding of other nanomaterials[5]. This nanoparticle system could greatly enhance the pharmaceutical efficacy of drugs, the sensitivity of biosensors and the success of biomedical therapies.

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Pt(IV) – Tyrosine Kinase Inhibitors: Potent dual-modal conjugates

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Side-effects due to the lack of selectivity toward cancer tissues is one of the major drawbacks to Platinum(II) anticancer agents (i.e. cisplatin, oxaliplatin). Nevertheless, despite these severe side-effects, platinum-based compounds remain one of the first worldwide choice to treat a variety of tumours. Tyrosine Kinases (TK) are promising targets in oncology and play a major role in cell regulation pathways. For example, overexpression of Platelet Derived Growth Factor Receptor (PDGFR) is associated with angiogenesis and metastasis in many tumour tissues. Imatinib, Nilotinib and Sunitinib are three well known clinically used drugs that can inhibit tyrosine kinases[1]. Herein we report a strategic synthesis for the formation of Pt(IV) pro-drugs with tyrosine kinase inhibitors conjugated in axial postitions[2]. Isolated enzyme-inhibition studies of each complex against PDGFRa indicate their utility as dual-modal conjugates. Finally, reduction studies of the complexes via ^{1}H NMR and Cyclic Voltammetry are shown followed by their preliminary cytotoxicity against cancer cell lines overexpressing PDGFR.

Acknowledgements
Irish Research Council for funding this research via a Government of Ireland Postgraduate Scholarship (GOIPG/2020/55).

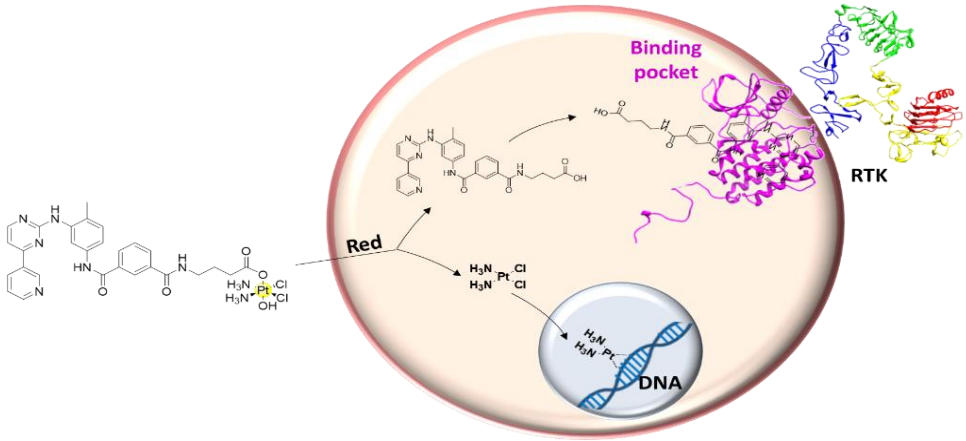

Figure 1. Intracellular reduction of general Pt(IV)-Imatinib pro-drugs

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NAPHTHALIMIDES EXHIBITING AGGREGATION INDUCED EMISSION FOR BIOIMAGING APPLICATIONS

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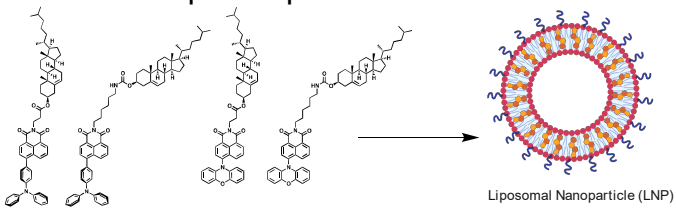
1,8-Naphthalimides (Naps) are highly versatile organic moieties that have been used in many different applications ranging from therapeutics, luminescent bioimaging agents, sensors, soft materials, and organic light-emitting devices.[1] A growing class of Naps are those exhibiting aggregation-induced emission (AIE)[2,3] which has rendered them useful, for example, as nitroaromatic sensors[4] or very recently as real-time lipid droplet imaging agents.[5] The latter example was built on Naps combining an electron donor-acceptor structure with multiple singly-bonded aromatic rotor groups, conferring AIE that could be visualised using fluorescence lifetime imaging (FLIM) as the dyes are delivered into cells and localise within the lipid droplets.



This project builds on this work by addressing three key areas: 1) photophysics; 2) biological properties; 3) dye delivery. Incorporation of stronger electron donors redshifts the emission and induces delayed fluorescent lifetime signatures that are identifiable with FLIM. Addition of cholesterol moieties generates dyes with specific targeting units for organelles such as the cell membranes, as well as facilitating the self-assembly process with polymer lipids to generate lipid nanoparticles (LNPs) capable of delivering the imaging agents to the cells.

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This work was supported by Science Foundation Ireland 18/EPSRC-CDT-3581 and the Engineering and Physical Sciences Research Council EP/S023259/1.

Developing Novel Re(I) Tricarbonyl Complexes as Antimicrobial and Anticancer Agents to Combat Drug Resistance

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The World Health Organization has declared that Antimicrobial Resistance (AMR) is one of the top threats facing humanity.[1] AMR is predominantly caused by the misuse or overuse of antimicrobial drugs. Resistance to commonly used anticancer treatments is also prevalent. This is concerning given that cancer accounts for 30% of deaths in Ireland.[2] Clearly new, unique therapeutics are needed to combat drug resistance.
Previously we have described the syntheses of two novel phenanthroline ligands, phenanthroline-oxazine and pyrido-phenanthroline (**Figure 1a**,**b**). [3] The latter is structurally related to ascididemin (**Figure 1c**), an alkaloid that is cytotoxic to cancer cells. [4] My research is centred on the development of rhenium complexes incorporating these ligands for their use in different medicinal applications. Tricarbonyl complexes of rhenium are particularly attractive due to their low *in vivo* toxicity [5] and have previously been evaluated as anticancer and antimicrobial agents. [6] This presentation will include the synthesis and characterisation of a series of tricarbonyl rhenium complexes in which the lipophilicity of the ligands is altered by increasing the length of the alkyl chain R (methyl, ethyl, propyl or hexyl) (**Figure 1d**,**e**). The activity of the complexes and the corresponding free ligands were studied against *S. aureus,* MRSA, *C. albicans* and ovarian cancer cell lines PEO1 and PEO4. We also describe some physical properties of the rhenium complexes including their redox couples, photoactivity and potential for ROS generation.

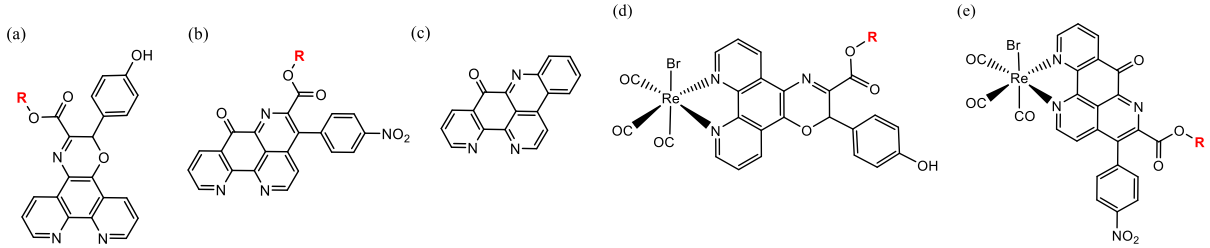

Figure 1: Structures of phenanthroline-oxazine (**a**), pyrido-phenanthroline (**b**), ascididemin (**c**) and Re(I) complexes of phenanthroline-oxazine (**d**) and pyrido-phenanthroline ligands (**e**).

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Integrating efficacy with characterisation: pioneering a novel target profile for topical antifungal solutions

O34

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A proprietary modified coconut oil formulation (MCO) has revealed notable antifungal efficacy against *Trichophyton rubrum*, an opportunistic pathogenic fungus affecting both the integumentary system and the nails. Process analytical measurements are providing insights into the specific properties of the oil, contributing to the broader understanding of its potential as a therapeutic agent and aiding the identification of its mechanism of action.

MCO's critical quality attributes undergo physiochemical, thermo-analytical, spectroscopic and chromatographic assessment. Efficacy is assessed via *in vitro* microbiological assays, enabling comprehension of antifungal properties, including dose extrapolation and fungicidal kinetics.

Physiochemical analysis has divulged distinctions between initial virgin coconut oil (VCO) and its modified counterpart. Attributable to altered colligative properties, both bomb calorimetry and differential scanning calorimetry effectively confirm the modification and thermodynamically differentiate the stages of manufacture. Infrared carbonyl stretching affirms characteristic modified variations within the 1700-1750 cm^{-1} region. The related Raman spectroscopy yields further subtle differences and correlates spectral data with compositional profile as determined using gas chromatographic FAMEs analysis. Calibrated experiments using lower-chained fatty acids (C8-C12) demonstrate notable inhibitory effects against the fungus. Batches of MCO consistently exhibit robust antifungal activity across *in vitro* bioassays, additionally outperforming a market-leading commercial product.

Reflecting the need to control the properties of naturally derived ingredients, validation of the coconut oil modification process through identification of its key effective components, holds promise as a potent contender for the antifungal market.

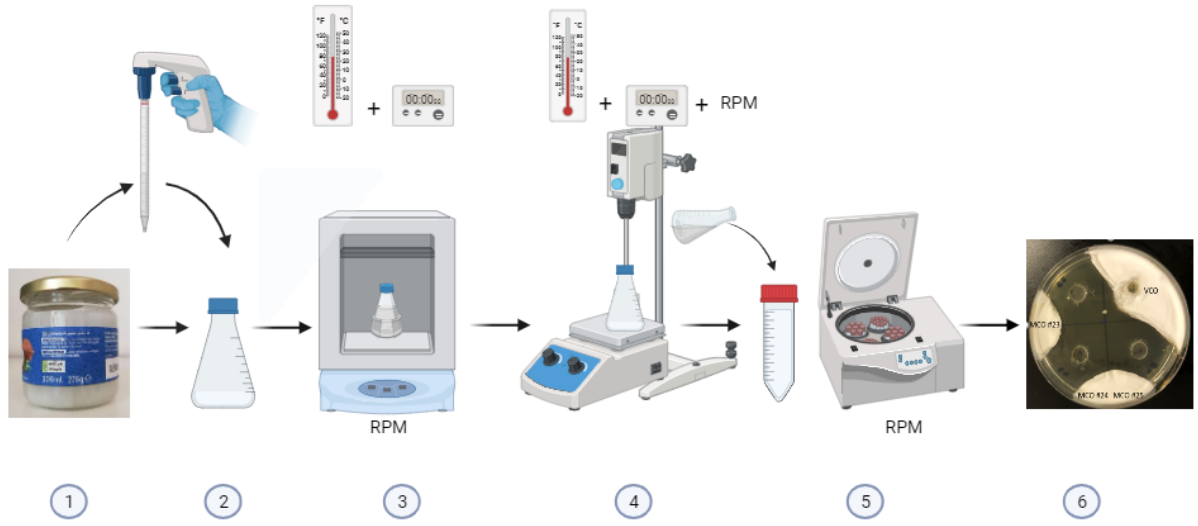

Figure: MCO manufacturing process resulting in fungal inhibition. Image: BioRender.

Unravelling the effects of solvents in the crystal nucleation of griseofulvin

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Crystallisation is a critical purification and manufacturing step for pharmaceutical companies. It starts with a nucleation stage: whose lack of control could lead to detrimental results. Unfortunately, the phenomenon remains poorly understood due to subtle balance between thermodynamic and kinetic factors as well as to the difficulty in detecting the early formation of small nuclei.

This research focuses on investigating the effect of solvents on the solid form and kinetics of crystal nucleation of griseofulvin (GSF). GSF is an active pharmaceutical ingredient used to treat fungal infections. Visual detection of the onset of nucleation was conducted in 20 mL *n*-butyl acetate (nBuAc), acetonitrile (ACN), and methanol (MeOH) solutions. These solvents were selected based on their solubilities (ACN ten times higher than the other solvents) and their molecular structure.

Powder X-ray diffraction indicated that GSF crystallised either as the stable form I in MeOH [1], as a previously reported solvate in ACN [2], and as a new solvate in nBuAc [3]. At room temperature and low humidity, the desolvation of the solvate with nBuAc forms the stable form I and with ACN forms a new polymorph, form VI [3]. This new polymorph is a relict host structure that emerges from the removal of the guest solvent related to several previously reported GSF solvates [3]. The discovery these new forms highlight the importance of polymorphism landscape and crystal form screening.

Kinetics analysis indicated that GSF nucleated faster in ACN, followed by nBuAc and then in MeOH. The nucleation rate increased with the increase in solubility, pre-exponential factor (A) and interfacial energy (γ). According to classical nucleation theory (CNT), the nucleation rate is inversely proportional to the interfacial energy and directly proportional to the pre-exponential factor [4]. Therefore, for GSF in the solvents analysed, the interfacial energy has a greater influence on the nucleation rate than the pre-exponential factor. This discrepancy between CNT and nucleation experiments highlights the complexity of this phenomenon, which requires further attention, especially for organic complex structures.

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Xanthines sulfate salts from tea and chocolate: a solid form landscape investigation

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University of Limerick, Bernal Institute, Limerick

The screening of the solid form landscape of a single molecule or ion is particularly important in many industrial sectors such as pharmaceutical, agrochemical, semiconductor, pigments etc. due the property differences that each solid phase can manifest.[1] For example, solubility and stability are of particular importance for drug manufacturing, storage and delivery; besides detrimental changes in these properties, spontaneous phase transformations can occur with salient movement of the solid particles (jumping crystals) and disintegration of the solid form.[2, 3]
Crystal engineering claims that supramolecular knowledge in the solid state enables the rational design of new crystal forms and properties; however, even simple chemical systems challenge this approach. In this regards xanthines, water and sulphate have been referred to as the nemesis of crystal engineering.[4-6]
Xanthines are alkaloids pharmaceutically active as adenosine blocker used for asthma and as stimulants. Theophylline and theobromine are the principal xanthines responsible for the stimulating effect in tea and chocolate respectively.
In this work new sulfate salts of theophylline and theobromine were synthesized by solvent evaporation and mechanochemically (manual grinding and ball milling) affording multiple polymorphs and hydrated. Characterization was carried out by X-Ray diffraction (SC-XRD and XRPD), thermal analyses (TGA and DSC) and electron microscopy (SEM).
Besides a rich collection of polymorphs and hydrated forms, it was observed that the thermal dehydration of theophylline hydrogen sulfate dihydrate occurs in a salient, rocket-like manner. At the same time an order disorder transformation was identified for the anhydrous theobromine hydrogen sulphate salt that might enable protonic conductivity at mild temperatures.

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Non-enzymatic sensing platform for *N*-Acetyl Neuraminic Acid based on electrodeposited boronic acid film on glassy carbon electrodes

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Sialic acids represent a family of molecules which can form part of a "sugar-coating" on the surface of human cells. This coating not only protects the cells, but interacts also with other cells. They play a role in brain development, central nervous system, human lactation and infant cognition and are often relevant in diseases like cancer, cardiovascular disease etc. [1] Bacteria and viruses can evolve to utilise sialic acids in order to evade the natural immune system in the body by producing sialylated lipopolysaccarides on their own cell surface, acting as an "invisibility cloak" to mask the host's immune surveillance system. Recently, a special form of sialic acid (sialyllactose) has been approved for use in commercial food products as a nutritional additive, e.g. to supplement infant formula to reach the levels of these species found in human milk [1]. For all these important reasons we are interested in developing sensors for measurement of such important molecules in a range of samples e.g. clinical, nutritional and dairy products.

To do this, we designed resourceful chemical materials which bind to these sugar molecules in a way that can be fine-tuned using control of the experimental parameters. These materials have a chemical group "tag" which accepts or donates electrons, allowing a readout proportional to the amount of sialic acid in a sample, an "anchor" which allows us to entrap it on a conducting surface and a "hook" or receptor group which is specific for the molecule we want to detect. In this work, we examined some promising receptor molecules based on boronic acids such as 6-Aminobenzo[c]xaborol-1-(3H)-ol hydrochloride (ABOXB). Following successful immobilisation of ABOXB through potential cycling, studies carried out at pH 4.5 indicated that the film's redox behaviour altered in the presence of increasing additions of Neu5Ac over the mM range; 100-800 µM, sensitivity 4.25×10^{-4} A M^{-1} **(Fig.1).** Film characterisation is underway via SEM/EDS, FTIR, spectroelectrochemistry in addition to electrochemical impedance spectroscopy and the use of pulse techniques to achieve a more sensitive response. Due to the monomer's bulky groups, steric hindrance prevents the formation of a uniform film, and we aim to employ an underlying NiO layer (possibly combined with reduced graphene oxide) in order to increase the surface to volume ratio and optimise the electrodeposition process for improved analytical performance.

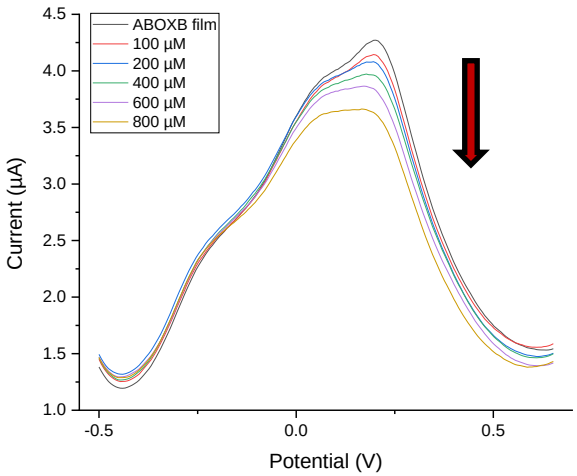

Fig. 1 Differential Pulse Voltammetry (DPV) of ABOXB film on Glassy carbon Electrode in pH 4.5 Acetate buffer in the absense and presense of 100-800 µM (graph shows three cycles ran for each addition averaged)

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Development and Characterisation of Poly(catecholamine) Surface Coatings

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Mussel Foot Proteins (MFP), enriched with the amino acid derivative L-DOPA (L-3,4-dihydroxyphenylalanine), exhibit remarkable adhesion to virtually any surface. Researchers have developed L-DOPA-modified polyols, oligomers, and polymers analogue to mimic the adhesive characteristics of MFPs using high concentrations of L-DOPA, addressing significant challenges in adhesion, antifouling, and surface modification. [1,2] Inspired by this natural adhesion mechanism, one interesting approach involves yielding functional coatings from small catecholamine adsorbates, where for example dopamine undergoes oxidative self-polymerisation to produce polydopamine coatings. [3]

In this work, three distinct functional molecules were modified with L-DOPA: tetrafunctional pentaerythritol (PE), bifunctional oligoethylene glycol (OEG), and monofunctional methoxy oligoethylene glycol (mOEG) to produce tetra(catecholamine) PE-DOPA, bi(catecholamine) OEG-DOPA, and mono(catecholamine) mOEG-DOPA, respectively. The derivatives characterised by Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetry/thermogravimetric analysis (DSC/TGA). These derivatives were then coated onto glass and stainless steel (SS) substrates via dip-coating under alkaline conditions at a concentration of 2 mg/mL for 18 h, resulting in poly(PE-DOPA),[4] poly(OEG-DOPA) and poly(mOEG-DOPA) adlayers. Subsequent thermal annealing of the coated substrates was conducted at 120°C for 6 h. Characterisation of all poly(catecholamine) coatings was performed using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and water contact angle (WCA) measurements.

The coating thicknesses, as determined by XPS, ranged from 1.0 to 4.0 nm on glass and 8.0 to 12.0 nm on SS. XPS further confirmed the presence of catecholamine molecules on the substrates, as evidenced by increased carbon and nitrogen signals alongside reduced substrate signals. Post-annealing, the nitrogen high-resolution spectra indicated the transformation of primary amine groups into secondary and tertiary species, likely attributable to significant indole ring formation. All as-coated poly(catecholamine) substrates exhibited enhanced hydrophilicity compared to bare substrates, as demonstrated by WCA measurements, with decreased hydrophilicity after annealing. Langmuir adsorption isotherm studies suggested monolayer formation on glass substrates and multilayer formation on SS substrates, likely due to catechol complexation with dissolved Fe^{3+}/Cr^{3+} metal centres.[5] AFM analysis indicated that tetrafunctional poly(PE-DOPA) layers exhibited higher RMS roughness values compared to bi- and monofunctional poly(OEG/mOEG) layers on SS (see Figure 1a). Figure 1 illustrates some plausible structures of poly(catecholamine) coatings on SS.

Moreover, the affinity of proteins, specifically bovine serum albumin (BSA), for both as-coated and annealed specimens was investigated using XPS. The interaction of BSA with the coated surfaces varied depending on the type of poly(catecholamine) coating and the environmental conditions, particularly the pH of the BSA dip-coating solution.

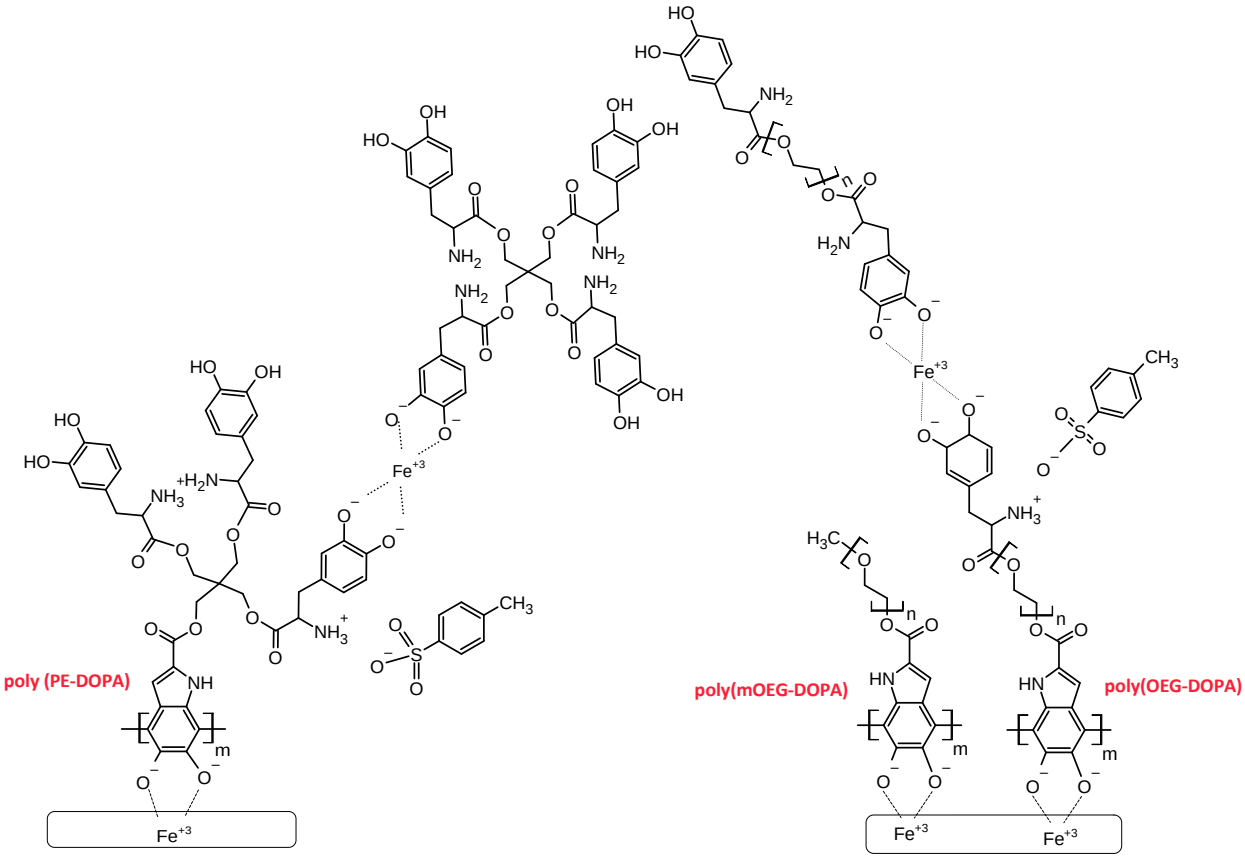

Figure 1. Proposed multilayer adsorption mechanisms for poly(catecholamine) coatings on SS, illustrating the coordination of unbound catechol moieties around dissolved Fe^{3+}/Cr^{3+} centres. [5]

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Abstracts Poster Presentations

Pt (IV)-DEVD-doxorubicin conjugates as dual action prodrugs for selectivity treatment of osteosarcoma

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Osteosarcoma is the main primary bone malignant entity affecting adolescents and young adults. Unfortunately, the rate of therapeutic response was not improved since decades and the survival of osteosarcoma patients remains very low, specifically for metastatic patients. The standard of care for osteosarcoma includes currently the chemotherapy agents cisplatin and doxorubicin (DOX).[1]
Unfortunately, their use is limited due to severe dose-limiting side effects and to overcome these issues, the scientific interest has moved toward the development of prodrugs that need to be activated on the target site, restoring the latent cytotoxic activity. One example are Pt (IV) species with a second biological prodrug as axial ligand that are dispatched and activated upon reduction.[2]
The real challenge in adding doxorubicin as the axial drug is that it should be released without structural modification and to achieve this goal a self immolative linker should be preferred. A recently developed cleavable peptide DEVD (Asp−Glu−Val−Asp) has been noted for being the substrate of caspase-3, which is upregulated in apoptotic cells. The conjugation of Pt (IV) complexes with doxorubicin using this specific peptide can be strategic for the delivering of such adducts; the intracellular reduction of Pt (IV) prodrug will cause the apoptosis which in turn will activate the caspase-3 that will release doxorubicin form the DEVD peptide. [3] The spacer between DOX and DEVD is p-aminobenzyloxycarbonyl, which is self-immolative, and not only provides systemic stability but also allows for selective release of intact DOX.

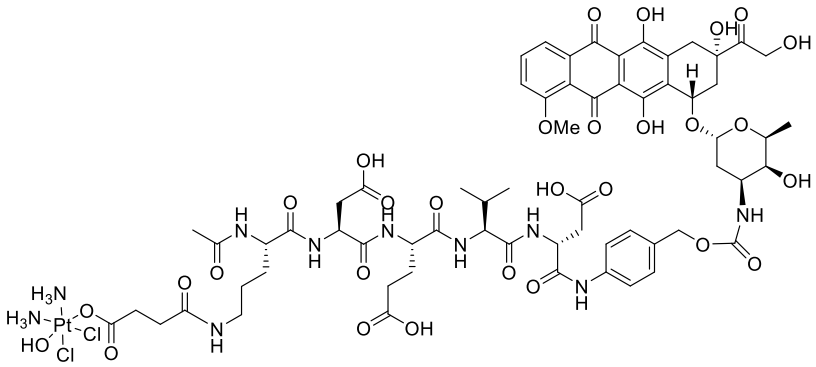

Figure 1. Structure of Pt (IV)-DEVD-S-DOX conjugate

Acknowledgments. Funding of this research by the STRIKE project HORIZON-MSCA-2021-DN-01 No. 101072462.

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High valent first-row transition metal halides complexes for oxidative halogenation of saturated hydrocarbons

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Classical industrial methods for halogenation of organic molecules tend to be highly energetically intensive and require the use of hazardous reagents such as halogen gases or halogen acids [1,2]. Due to the high demand for halogenated products in most areas of chemical industry, the need for cleaner and less harmful halogenation processes is of great urgence.

Nature employs enzymes to perform oxidative functionalisation of various organic substrates. One important example is Heme Haloperoxidase [3], which contains a heme-Fe centre whose reactivity revolves around the formation of high-valent iron-oxo species, which can functionalise organic C-H bonds through a process of Hydrogen Atom Transfer (HAT) followed by Radical Rebound.

Since the main driving force of the HAT process is the Bond Dissociation Energy (BDE) of the O-H bond that is formed in this step, we propose that replacing the metal-oxo species with a metal-halide species, the main driving forces will become the BDEs of the H-X bonds (X = F, Cl), which are reportedly higher that the ones for O-H bonds, allowing us to cleave even stronger C-H bonds, such as the ones of saturated hydrocarbons. To achieve this, we are preparing a series of first-row transition metal porphyrin-complexes, with the metal in the M(III) oxidation state bounded to a halogen atom (F or Cl) (Figure 1a). From these precursors we are generating *in-situ* the corresponding M(IV) di-halide species (Figure 1b). Preliminary data suggest that these species can react in presence of organic substrates and perform the cleavage of saturated C-H bonds (Figure 1c).

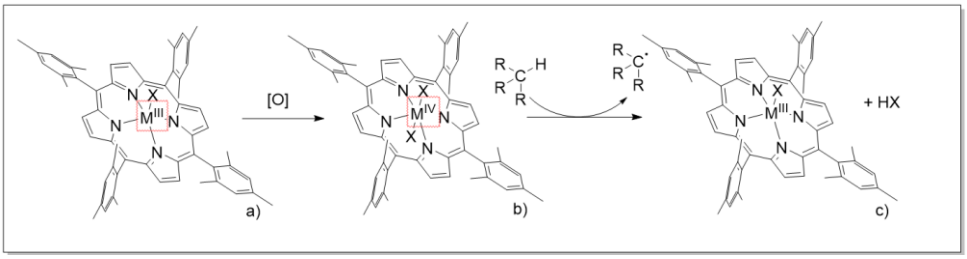

Figure 1: a) Metal-Halide porphyrin complexes used in this study. General formula M(III)TMPX [M = Fe, Mn, Co; TMP = 5,10,15,20-Tetrakis-(2,4,6-trimethylphenyl)-porphyrin; X = F, Cl]; b) In-situ generated high valent metal-halide species.; c) HAT process performed by the in-situ formed high valent species.

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Development of Biocompatible Graphene Oxide-Based Magnetic Nanoplatforms for Targeted Drug Delivery

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Two-dimensional graphene and its composite nanomaterials exhibit remarkable physical and chemical properties, which have been extensively investigated across various fields in recent years [1]. Moreover, developing multifunctional theranostic platforms with synergistic capabilities has garnered considerable attention. The study presented here aims to create a multi-functional biocompatible magnetic-responsive graphene oxide-iron oxide nanoplatforms for the targeted delivery of anticancer drugs to treat osteosarcoma. Initially, superparamagnetic Fe_3O_4 nanoparticles are synthesized using the co-precipitation method [2]. To achieve biocompatibility and high physiological solutions stability, these nanoparticles are coated with polydopamine (PDA), which provides functional groups enabling further modifications [3]. The microstructure and physical properties of Fe_3O_4/PDA nanoparticles and GO were investigated by Raman spectroscopy, Fourier transform infrared spectroscopy and Scanning electron microscopy. Structural analysis of graphene oxide via Raman spectroscopy reveals a highly disordered structure ($I_{D/G}$ = 0.99) [4] and confirms that magnetite is the iron oxide phase present in the sample. After coating, PDA's catechol groups introduce new features in Raman and FTIR spectra, confirming the presence of the PDA film on the surface of magnetite nanoparticles. Morphological analysis shows that Fe_3O_4@PDA nanoparticles are spherical, smooth, and approximately 130 nm in size. Future work will focus on the further development of these 2D magnetic nanoplatforms for loading and delivering single or multiple therapeutical agents.

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Synthetic Magnesium Tetrapyrroles for Mechanistic Studies of Photosystem II

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Magnesium tetrapyrrole derivatives are fundamental to the reactivity of several photosynthetic pigments, most notably the chlorin complex chlorophyll-*a* in P680 [1]. The P680 reaction centre consists primarily of 4 chlorophyll-a molecules. This gives an overall redox potential of 1.1-1.3 V (vs. SHE) whilst isolated chlorophyll-*a* in vitro has only shown potentials around 0.7-0.8 V [2]. Water oxidation reactions typically require extreme conditions and precious metal catalysts to work [3], yet photosynthesis occurs under ambient conditions. Taking inspiration from biology, elucidating the conditions and the mechanisms which allow chlorophyll to generate such high redox potentials under mild conditions may lead to ground-breaking improvements in oxidation catalysis.

A series of magnesium porphyrin and chlorin surrogates for chlorophyll-*a* are synthesised. The oxidation of these to π-cation radicals is carried out via chemical and electrochemical methods. The radical species are then studied by EPR and UV-Vis spectroscopy to optimise the generation of these. After probing the π-cation radicals, their oxidation reactivity towards phenol substrates is investigated via time-resolved UV-Vis spectroscopy. Our promising initial results are presented here including the synthesis of previously uncharacterised π-cation radicals, optimisation of their synthesis and demonstration of their reactivity towards a range of substrates. Ultimately, we aim to develop our findings into a mechanistic understanding of the influence of the tetrapyrrole ligand on natural oxidation chemistry.

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Utilisation of waste products for the construction of alkenes

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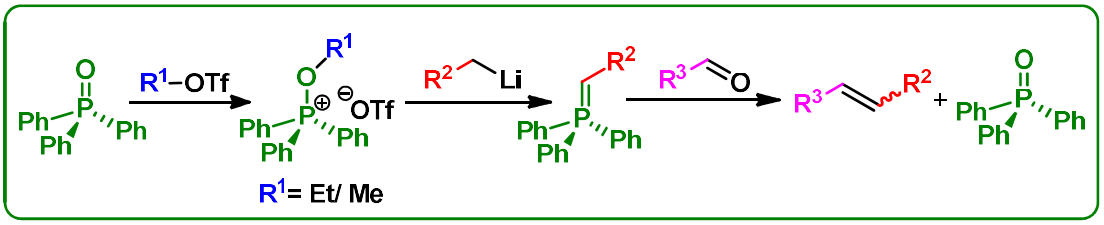
The formation of carbon-carbon double bonds is a key transformation in organic synthetic chemistry. The Wittig reaction[1] is the most frequently employed and general methods for the chemo- and regioselective preparation of alkenes. Nonetheless, the Wittig reaction suffers from several drawbacks. In particular, the separation of the phosphine oxide by-product can be challenging, impacting the purification of the alkene product.[2] This project focuses on utilizing phosphine oxide the typical waste product formed in Wittig reactions to form phosphonium ylides, crucial reagents in Wittig reactions and then using the ylides formed to effect Wittig reactions. Phosphine oxides are activated using alkyl triflates, producing alkoxyphosphonium salts.[3] Alkyllithium reagents then undergo nucleophilic substitution reactions on alkoxyphosphonium salts, forming quaternary phosphonium alkoxide salts. The alkoxyphosphonium ion is deprotonated by its alkoxide counter-anion to produce phosphonium ylides, enabling subsequent Wittig reactions with aldehydes. The alkyl triflate serves as both an alkylating agent and the source of the alkoxide base. Since Ph_3PO is both the starting material and the by-product of this process, this demonstrates that Wittig reactions using only catalytic quantities of phosphine oxide are in principle possible.



This methodology demonstrates that a broad range of aryl and heteroaryl aldehydes can be efficiently converted into alkene products with moderate to high yields using phosphine oxide as the starting material. In my project, conditions have been established to conduct Wittig reactions with stoichiometric amounts of phosphine oxide, leading to the synthesis and isolation of various alkene products. This approach is valuable because it enables the utilization of phosphine oxide, which would otherwise be a waste product, and it validates the feasibility of Wittig reactions using phosphine oxide as a catalyst.

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Development of Synthetic Routes to Novel Sulfur-Based Antivirals

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The Human Immunodeficiency Virus (HIV) is the pathological agent responsible for HIV infections. HIV attacks the hosts immune systems helper T cells which express the glycoprotein cluster of differentiation 4 (CD4) on their surface.[1] Gradual failure of the immune system due to the depletion of CD4 cells allows opportunistic infections to thrive where progression of HIV to Acquired Immunodeficiency Syndrome (AIDS) is likely. HIV/AIDS can be fatal. The major challenge in tackling HIV is found in its rapid mutation rate which drives resistance to existing antivirals. While the use of combination therapies has generally proven successful in treating the disease, new effective antiviral agents are continually required to combat future resistance. Nucleoside reverse transcriptase inhibitors (NRTIs) are a class of HIV antivirals which inhibit the enzyme reverse transcriptase. The acyclic nucleoside phosphonates (ANPs) represent a particularly interesting subclass.

Adefovir dipivoxil (**1**) is a well-known ANP prodrug of adefovir (**2**) (Figure 1). The *S*-acetyl thioethyl (SATE) derivative (**3**) of adefovir likewise shows enhanced bioavailability when compared to **2**.[2] This project focuses on the synthesis of novel, sulfur-containing SATE derivative **4**. Existing ANPs such as adefovir dipivoxil (**1**) contain phosphorus-oxygen bonds which are cleaved upon incorporation of the antiviral into the growing viral DNA chain.[3] SATE-derived antiviral **4** incorporates phosphorus-sulfur bonds which are more labile than phosphorus-oxygen bonds. This strategic bioisosteric replacement should allow for more rapid cleavage of the phosphorus-sulfur bonds and faster incorporation of the antiviral agent into the growing DNA chain.[4] Presented here is a summary of our work to date, including a variety of routes explored to reach target compound **4** through both the synthesis of phosphonodithioates and the derivatisation of adefovir (**2**).

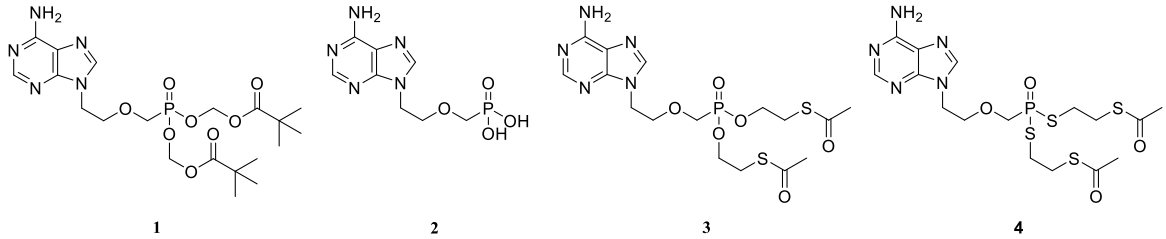

Figure 1

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Exploring Metal-Organic Frameworks as Catalysts in the Synthesis of Methyl Acrylate from CO_2

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CO_2 is normally seen as an inevitable waste product. However, CO_2 can be a source of C1 building block and could become a cheap raw material for different bulk chemicals such as methyl acrylate and acrylic acid derivatives, giving us the chance to turn spent-CO_2 into working-CO_2. The synthesis of methyl acrylate from the transition metal-mediated direct coupling of CO_2 and ethylene is an attractive approach for the reduction and reutilization of CO_2. At present, the synthesis is limited by its low yield which makes the reaction economically unsustainable.[1] This project combines in-silico design with in-vitro synthesis to identify a new material (i.e., a catalyst) that will make the reaction favourable. These new materials are sought within metal-organic frameworks (MOFs). Due to their crystalline, highly porous, and easily tuneable structures, they offer unique environments for the immobilization of active catalytic species.[2] UiO-66 is a zirconium-based MOF known for its remarkable thermal, chemical, and mechanical stability. This work focuses on functionalising defective missing cluster UiO-66 with commercially available amino acids to create a new super-efficient catalyst for this reaction.

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Tackling Antimicrobial Resistance *via* Novel BDSF Quorum Sensing Inhibitors

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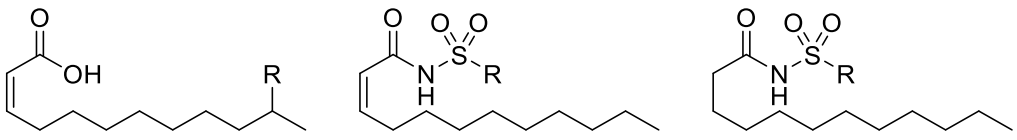
By 2050, 10 million people are expected to die each year as a result of resistant infections.[1] Traditional antibiotics are being rendered increasingly ineffective as bacterial resistance becomes more widespread. One strategy to combat AMR involves the disruption of native bacterial communication, known as quorum sensing (QS). The diffusible signal factor (DSF) family is a family of QS signals which have been found to control biofilm formation and virulence in many bacteria e.g. *Pseudomonas aeruginosa* and *Xanthomonas campestris*.[2] DSF (**1**) and *Burkholderia* DSF (BDSF) (**2**) are two important QS signals which are often found in the airways of cystic fibrosis (CF) patients (Figure 1).[3]

Our group has previously demonstrated how *cis*-unsaturated sulfonamides (e.g. **3**) can successfully inhibit QS in DSF-sensitive bacteria.[4] In this project, we have removed the *cis*-unsaturated double bond and generated a diverse library of saturated *N*-acyl sulfonamide isosteres of BDSF (**4**). These compounds will be subsequently tested for their ability to regulate DSF-dependent phenotypes, growth characteristics, biofilm formation and virulence. This will determine the importance of the presence of the *cis*-unsaturated double bond on the QS activities in the selected bacteria.



1 DSF : R = Me
2 BDSF : R = H

3

4

Figure 1

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Investigation of a synthetic route to aromatic Resolvins

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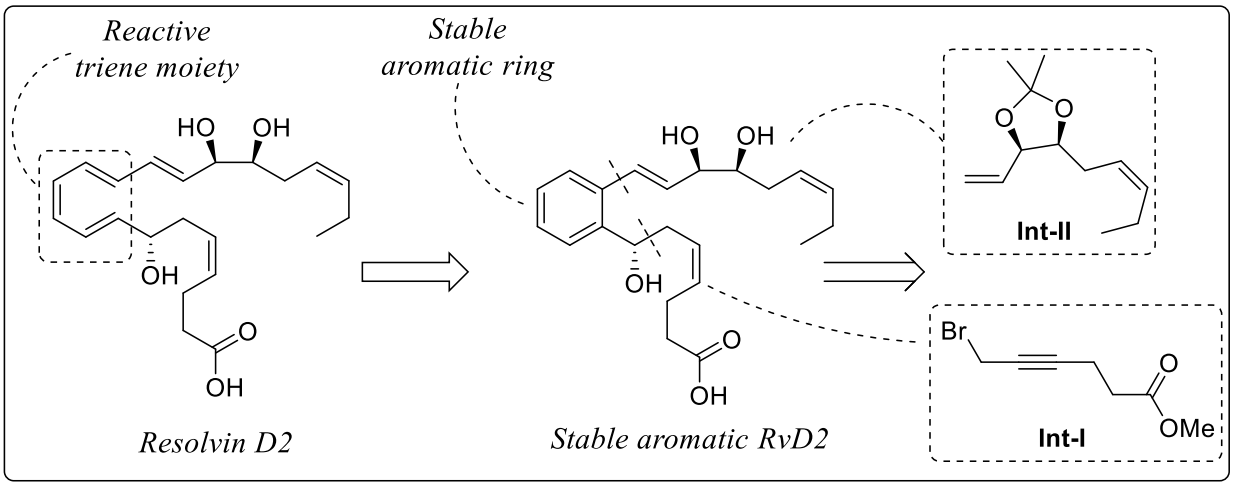
The Resolvins are a series of endogenous pro-resolving mediators with therapeutic potential for chronic inflammation [1]. Resolvin D2 (RvD2) is active at nanomolar concentrations, resolving inflammation by reducing neutrophil recruitment, cytokine production and bacterial burden. Although RvD2 is highly potent, its use as an anti-inflammatory drug is limited by a short half-life and challenging synthesis. This is partly due to the presence of a reactive triene system, which is prone to isomerisation and metabolic degradation.

In an effort to develop stable equivalents which retain anti-inflammatory activity, we designed aromatic analogues of RvD2. Replacement of the reactive triene core structure with a benzene ring should improve both molecular stability and ease of synthesis. Presented here is the synthesis of two subunits of an aromatic RvD2 analogue. The synthesis of **Int-I** involves addition of a protecting group, Grignard and Appel reactions, oxidation and alkylation steps [2]. Preparation of **Int-II** involves an initial protection step followed by two Wittig olefinations, and a Dess-Martin oxidation [3]. Subsequent coupling of **Int-I** and **Int-II** would constitute an efficient, convergent synthetic route to aromatic RvD2.



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Development of Pt-PROTACs to degrade Pt-binding Proteins

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Platinum (Pt)-based drugs such as cisplatin, carboplatin and oxaliplatin play a very important and well-documented role in treating cancer and are employed in nearly 50% of all anticancer treatments. The primary mechanism of Pt-based drugs is associated with their ability to cross-link nuclear DNA; the Pt-DNA adducts interrupt transcription, generate DNA perturbation damage responses and ultimately induce apoptosis. Pt(II) anticancer drugs also interact with a range of other nucleophiles, including RNA, mitochondrial DNA and proteins. Of these, the role Pt protein binding plays in on- and off-target activity of Pt-based drugs has been of particular interest. [1]

Proteolysis-targeting chimeras (PROTACs) are bifunctional molecules that have shown great promise in the identification of novel protein targets, and as therapeutic agents in clinic. They achieve this through hijacking the ubiquitin proteasome system (UPS) to achieve degradation of proteins of interest. [2] Our group recently described the first example of a metallo-PROTAC, showing that the complex could successfully degrade known Pt-binding proteins. [3] Building on this work, our group is currently designing a series of novel Pt-PROTACs for use in proteomic analysis. This will allow the identification of novel Pt-binding proteins and assist in unravelling the complex mechanisms of action associated with Pt-drugs. Progress in the design, synthesis and evaluation of these Pt-PROTACs will be presented.

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Enantioselective Intramolecular C-H Insertions of α-Diazosulfonates

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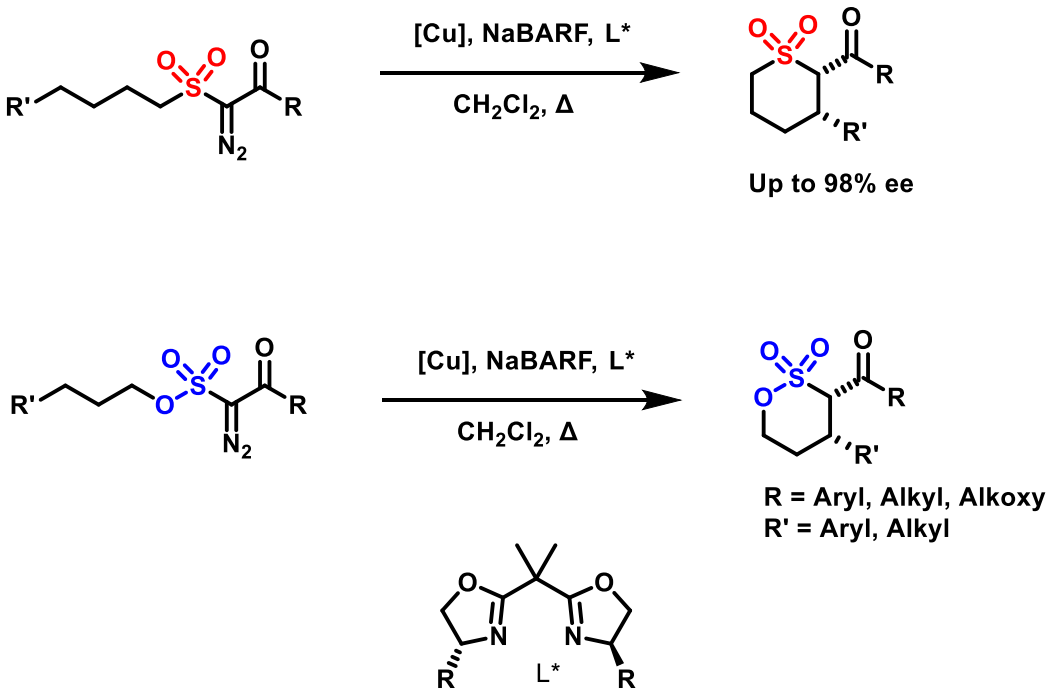
The Maguire-Collins team has published a series of papers over the past decade describing highly enantioselective intramolecular C-H insertions reactions in α-diazo-α-sulfonyl esters and ketones using copper bisoxazoline catalysts, based on readily available ligands.[1,2] Excellent enantiocontrol was obtained in the synthesis of thiopyrans from α-diazosulfones.[1,2] This work will explore if the enantioselective copper mediated C-H insertion can be effected with α-diazocarbonyl compounds where the sulfonyl moiety is replaced by a sulfonate moiety. The long term objective of this work is the formation of new C-C bonds with excellent control of absolute stereochemistry at both carbons.



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Development of green-based coatings with anti-corrosion properties

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The corrosion of metals and alloys is a natural phenomenon that has occurred over centuries, but it is becoming more of an impelling issue as the release of metal ions from corroding surfaces leads to environmental contamination. Furthermore, with the emphasis on renewable energy and offshore wind farms, corrosion in marine and offshore platforms, and pipelines is becoming increasingly important. The corrosion of these marine structures does not only lead to structural failure and costly repairs, but also contamination of seawater which will bring potential environmental disasters [1].

The application of organic coatings to metallic-based structures is the traditional corrosion protection method. However, the processing of these coatings relies on solvents and organic components, that are no longer environmentally acceptable and have additional health concerns. Furthermore, organic coatings can be defective with poor adhesion, lack of barrier properties, and inadequate chemical resistance, which allows the corrosive species to penetrate and reach the metal substrates. Accordingly, alternative green materials are urgently needed in corrosion protection systems [2].

In this study, a combination of three green material families, including (1) layered double hydroxides (LDHs), (2) green corrosion inhibitors, and (3) biopolymers were used to develop novel coatings with anti-corrosion properties. The synthesized LDHs were intercalated with green corrosion inhibitors while the biopolymers, derived from renewable sources, were applied as a sustainable alternative to traditional polymers. Moreover, the dispersion of green corrosion inhibitors into the biopolymer matrix creates a hybrid coating system exhibiting enhancement in corrosion protection and durability. In the context of chemical and electrochemical characterization, coating systems were analysed using SEM, EDS, XRD, potentiodynamic polarization curves (PDP) and electrochemical impedance spectroscopy (EIS). The findings showed that the developed green coatings have promising potential in corrosion protection. Not only do they lead to a significant reduction in the corrosion current density but are also cost-effective and environmentally friendly solutions for protecting structures against corrosion.

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Intermolecular C-H Insertion Reactions of α-Diazosulfones

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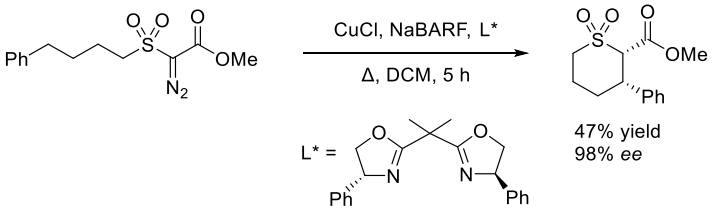
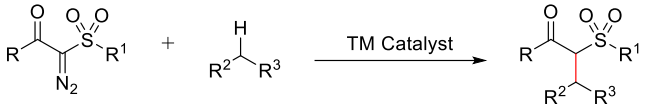
The Maguire-Collins group have published a series of papers over the past decade describing highly enantioselective intramolecular C-H insertions in α-diazosulfonyl esters and ketones leading to tetrahydrothiopyrans, sulfolanes, cyclopentanones, β-lactams and γ-lactams using copper bis(oxazoline) catalysts.[1–4] In the original 2010 report by the Maguire group, highly enantioselective intramolecular copper catalysed C-H insertion reactions of α-diazosulfones to form tetrahydrothiopyrans were achieved.[4]



Scheme 1: *Asymmetric copper catalysed intramolecular C-H insertion.*

The aim of this project is to explore powerful new methodology for the formation of new C-C bonds with excellent enantiocontrol, thereby adding to the toolbox available for enantioselective synthesis. Key to this methodology is the selective activation of previously unactivated C-H bonds through use of a catalyst with insertion of a carbene derived from an α-diazosulfone precursor.



Scheme 2: *Intermolecular C-H insertion reaction.*

Recent promising results have shown that it is possible to extend these copper catalysed C-C bond formations to enantioselective intermolecular C-H insertions for the first time (Scheme 2). The exploration of the impact of variation of the substrate and C-H source on the efficiency and selectivity of these transformations is discussed as well as examining the role of the catalyst, ligand and counterion in the C-H insertion step.

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Electrochemical Detection of Ornidazole by means of Copper-Iron nanoparticles and Carbon Black-modified electrode

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Antibiotics have become fundamental tools in our fight against disease but their accumulation in the aquatic environment due to discharges from manufacturing plants, hospitals and farms, and to misuse by the public has seen them emerge as water pollutants. Their presence constitutes a serious environmental and health risk due to their toxicity and due to the risk of antimicrobial resistance (AMR), which may render antibiotics ineffective when employed to fight infection. Assessing the impact of antibiotic pollution on water quality, drinking water, recreational/bathing water, and the impact on life is critical for our health and wellbeing.

Ornidazole is a member of the nitroimidazole antibiotic family that is heavily employed in the treatment of both human and animal infections [1]. This widespread use has led to the accumulation of the antibiotic in aquatic environments, posing a serious health risk due to its toxicity and the risk of AMR [2]. For this reason, novel and environmentally friendly methods of rapidly and accurately detecting its presence in the environment are vital to mitigate its pollution and harmful effects.

In this study two materials are combined to enhance the conductivity and ability of a glassy carbon electrode sensor to detect ornidazole. Carbon black, a material composed of 95% carbon with a structure similar to graphite [3] is functionalised using a novel green method with tannic acid. This is then combined with a layered double hydroxide (LDH) to act as a source of metal nanoparticles. LDH's are a combination of transition metals with the general formula $[M_{1-x}^{2+}M^{3+}_{x}(OH)_2]^{x}+(A^{n-})_{x/n}.mH_2O$ where M is two different metals and A is the intercalated anion between the stacked layers of M^{2+}/M^{3+} ions to produce a 2D layered nanosheet structure [4]. These LDHs are synthesised hydrothermally, which involves combining sources of the desired metals into a sealed autoclave and heating to produce a high vapour pressure environment.

Functionalised carbon black was dispersed and drop-casted onto the surface of the electrode. After drying, it was decorated by means of drop-casting with a dispersion of the LDH containing the desired elements. The LDH is then easily reduced by means of cyclic voltammetry to embed the nanoparticles of the desired elements into the carbon black, producing a stable modified electrode. LDH's containing a variety of elements were investigated for their ability to detect ornidazole. The optimum element combination was concluded to be copper-iron nanoparticles. The procedure for the synthesis and modification of the electrode can be seen in Figure 1.

The carbon black-copper iron (CuFe) modified sensor shows excellent sensitivity compared to bare glassy carbon and is capable of detecting ornidazole concentrations from 0.2 uM to 600 uM, displaying excellent stability over multiple uses. Studies were performed to characterise the carbon black-CuFe material using SEM, XRD, XPS, FTIR, and EDX. Investigations were carried out into the behaviour of the sensor at varying pH values and to

determine the reaction kinetics of detection. To study the selectivity of the sensor interferants were introduced to the antibiotic solution and experiments were performed in real water samples gathered from various locations.

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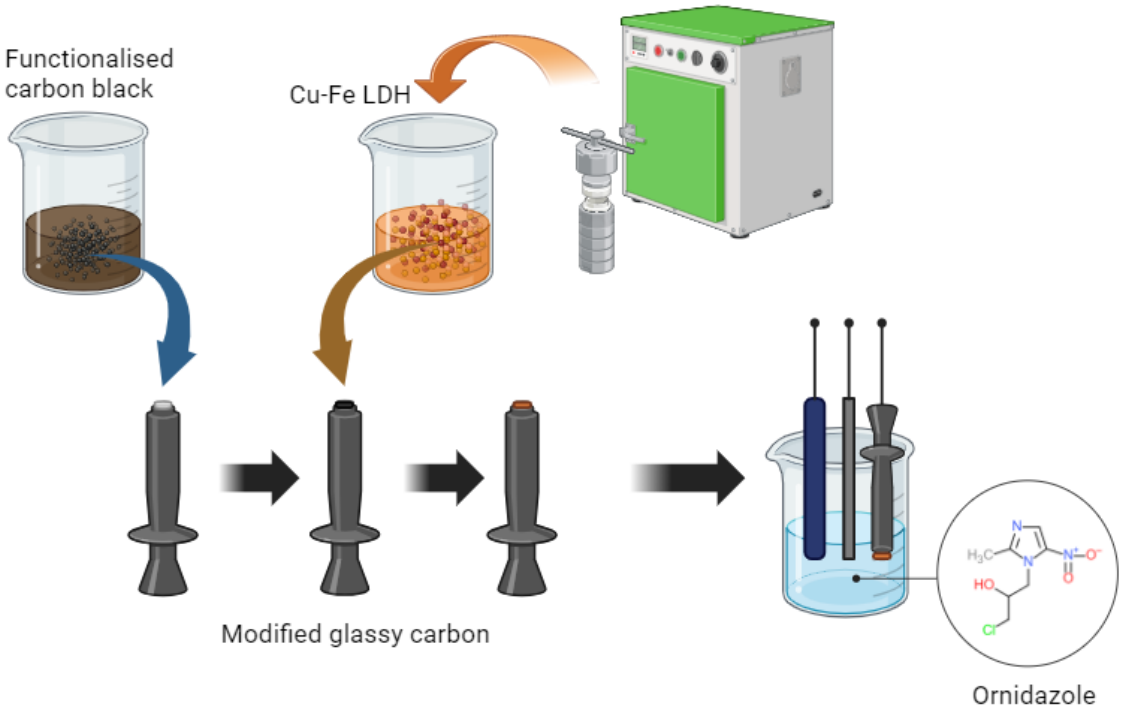

[5]

Bifunctional Layered Double Hydroxide Electrocatalysts for Water Splitting

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Water splitting is an area of research which is of pressing interest in addressing climate change. Water splitting provides oxygen and hydrogen as products, with hydrogen finding use as a potential high-density fuel to replace fossil fuels. Water splitting manifests as two half-cell reactions, namely the anodic oxygen evolution reaction and the cathodic hydrogen evolution reaction. The purpose of this project is to synthesise a bifunctional electrocatalyst to use in the water splitting reaction, replacing the rare and expensive transition metals catalysts currently in use such as platinum and ruthenium. In this project Layered Double Hydroxides (LDHs) have been synthesised for use in water splitting. The synthesis developed is a simple, one pot hydrothermal synthesis. The LDHs have been characterised and their structure confirmed by a variety of analytical techniques including X-Ray Diffraction and Scanning Electron Microscopy. A variety of metallic salts have been tested for their use in these LDHs with the optimum LDHs selected for further study. These LDHs have been immobilised on a variety of porous, high surface area materials, for example nickel foam and copper foam, to enhance the properties seen in the screening study. To enhance the stability of the LDHs, carbon materials have been added during the hydrothermal synthesis process.

Carbon Dioxide Utilisation for Construction of High Value Carboxyl-Containing Organic Products

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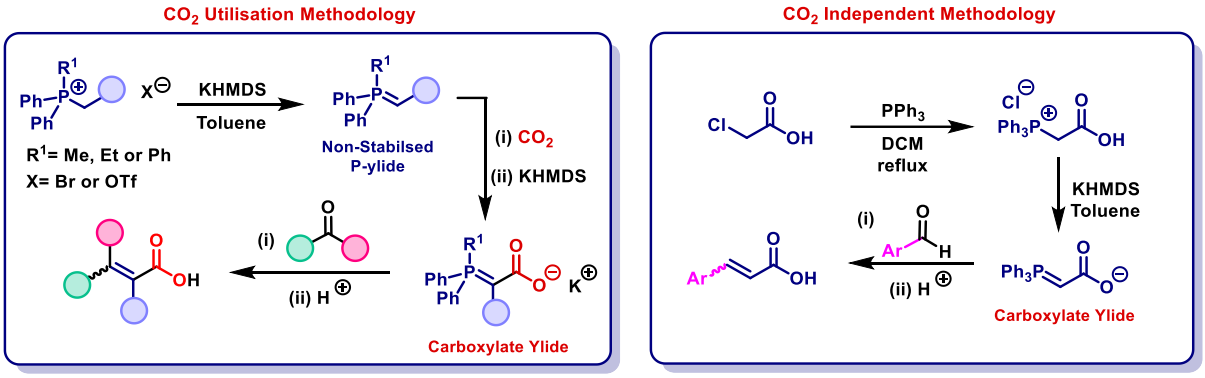
Employing waste products as starting materials for chemical transformations is a key step in addressing the global challenges of sustainable production and consumption. The greenhouse gas CO_2 is perhaps the most significant waste product of the industrialised world.[1] Developing a method for the conversion of a harmful environmental waste product into carboxyl-containing organic products can allow CO_2 to be used as a one-carbon (C1) chemical building block. Phosphonium ylides (P-ylides) have the ability to activate CO_2 into reactive P-ylide CO_2 adducts.[2,3] This activated form of the C1 feedstock can be incorporated into high value carboxyl-containing products and biologically active compounds.

α,β-Unsaturated carboxyl containing organic products are ubiquitous in nature and this structural motif is responsible for the biological activity of many such organic products.[4] It has been found that α,β-unsaturated carboxylic acids can be synthesised using two comparable synthetic routes. The CO_2 utilisation methodology involves the in-situ generated P-ylide activating gaseous CO_2, forming the P-ylide CO_2 adduct. A novel Wittig reaction occurs between the P-ylide CO_2 adduct and aromatic, heterocyclic, and aliphatic aldehydes as well as ketones, forming α,β-unsaturated carboxylic acids in moderate to high yields. This telescoped process has shown a high degree of selectivity for the *E*-alkene. Included among the substrates synthesised were pharmaceutical intermediates, strengthening the synthetic value of the process. Isotopic labelling is also possible with this methodology.



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Asymmetric Synthesis Using Transaminases as Biocatalysts

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University College Cork

Use of biocatalysis is a very powerful approach in enantioselective synthesis, aligning with many of the Principles of Green Chemistry.[1] In this work, the synthetic potential of three transaminases, two novel marine (P-ω-TA and P-ω-TAad2) and one previously described (Cv-ω-TA), are explored for the synthesis of amines closely related to APIs. Collaboration with the O'Gara and Reen groups in molecular biology is key to this research, in providing access to novel enzymes which have not been previously explored in synthesis.

Recent results from the kinetic resolution of racemic amines utilising novel transaminases will be presented.The novel marine transaminases displayed excellent activity and remote diastereoselection in the kinetic resolution of norsertraline, a structural analogue of the API Sertraline.[2] Expansion of the substrate scope is described together with discussion of the impact of structural alteration on the efficiency and stereoselectivity of the biocatalystic step.[3]

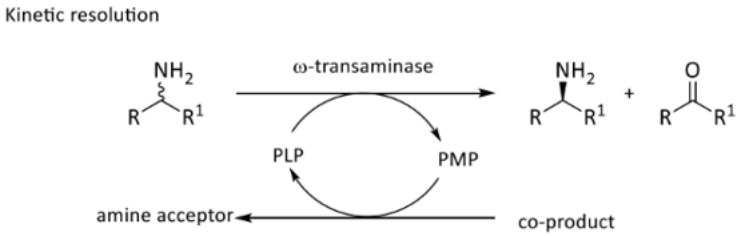

Figure of Transaminase mediated kinetic resolution

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Model Compounds for the Investigation of Electrostatic Effects in Photosynthetic Pigments

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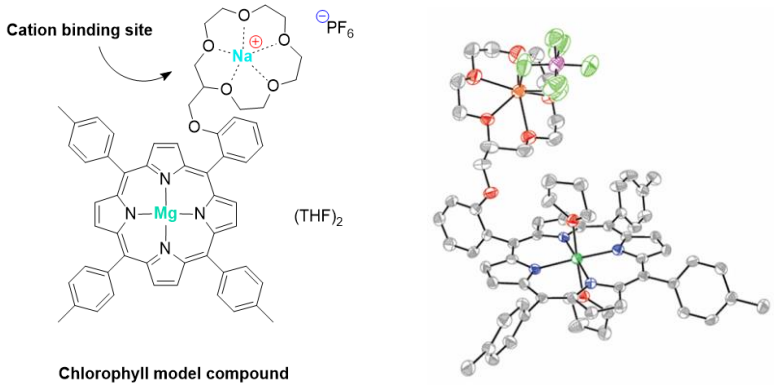
Photosynthetic water oxidation is catalysed by the enzyme Photosystem II (PSII). The reaction is initiated by 1-electron photo-oxidation of a chlorophyll-a tetramer named P680. The product is a π-cation radical complex, P680+, with an exceptionally high redox potential of 1.1 - 1.3 V vs SHE. This species drives water oxidation by oxidising the oxygen evolving complex via a tyrosine residue. [1] The extreme redox potential of P680+ renders it the most potent oxidant in biology, a fact that is especially interesting considering the comparatively diminished redox potentials of monomeric chlorophyll-a and other related photosynthetic pigments (0.45 - 0.78 V vs SHE). [1, 2] The origin of the high redox potential of P680+ is unknown, but a number of proposals have been put forward in the literature, such as: the nature of axial ligands at Mg, the relationship between different chlorophyll molecules in the pigment, and the electrostatic/dielectric environment of the surrounding protein. [3, 4, 5] Uncovering the factors that contribute to the high reactivity of P680+ promises to both improve our understanding of water oxidation in PSII and unearth new design principles for synthetic oxidation catalysts.

This work aims to address the last of the above-listed postulates by demonstrating the impact of electrostatic interactions on the redox and reactivity properties of chlorophyll model compounds. To this end, we have synthesised and characterised crown ether appended Mg porphyrins, their adducts with redox-inactive metal cations and their 1-electron oxidation products in the presence/absence of bound cations, allowing us to assess the impact of electrostatic potentials on bio-relevant reactivity.



Chlorophyll model compound

References:

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Carbon-negative construction materials from a biorefinery

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Carbon dioxide has been emitted to the atmosphere in ever-increasing quantities for the past hundred years, ultimately resulting in climate change. Two industries are major contributors to these emissions and both are foundational industries to the global economy: the petroleum and the construction industries.

Our research intents to replace the raw materials from the petroleum industry with bio-based alternatives from waste lignocellulosic biomass (LCB), and to use the construction industry to economically remove and store carbon from the atmosphere. To do so, my project is divided into two steps.

The first phase aims to develop a new LCB pretreatment process, based on the use of novel green solvents and blends. Indeed, they are known to be a key determinant in the pretreatment, influencing the properties of the obtained biomass precursors [1], [2], [3], [4]. Solvents behaviours in classic processes were thus analysed, to identify the ideal properties of pretreatment solvents [1], [2], [3]. This study was coupled with experimental investigations and software modelling using the Hansen Solubility Parameters.
The solvent sequence will yield hemicellulose, lignin and cellulose, which are the bio-based platforms for novel polymer. Lignin is particularly interesting as its properties can be tuned during pretreatment depending on the solvents and auxiliary reagents employed [1], [2], [3], [4].

The second phase of our project will involve converting these three platforms into novel high-value polymers, to replace common materials used in the construction industry, like concrete, steel or petroleum-based plastics [4]. These polymers will be tested for properties such as tensile, compressive or shear strengths and compared with the current materials ones.

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Towards tumour theranostics: hypoxia activation as a tool for therapy and diagnostics

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Hypoxia, a diminished availability of molecular oxygen in bodily tissues, has long been a therapeutic target for cancer research given its major role in tumour growth and resistance to therapy.[1] Moreover, despite an explosion of information on hypoxia and its role in tumour development, there are still major questions to be addressed if the long-standing goal of exploiting tumour hypoxia in diagnostics and therapy are to be realised.[2,3] Effective approaches to reliably detect and image hypoxic areas within tumours are therefore critically required.[4] This work will outline our recent approaches to achieving 'Smart Theranostics' by the synthesis of activatable magnetic resonance imaging (MRI) agents. Our approach relies on a series of reductive enzymes upregulated at the site of hypoxic stress that provide an activation pathway of the agent predominantly available at a site of hypoxia. This presentation will focus on our initial synthetic efforts towards a series of mixed Ln(III) MRI contrast agents that we expect will display 'switch on' behaviour under hypoxic conditions.

The proposed research will develop a series of theranostic agents that will be selectively activated in the hypoxic tumour microenvironment.[1,2] We will achieve this goal through a bioconjugation approach where vector peptides will be conjugated to an enzymatically responsive MRI contrast agent and therapeutic drug. The final goal is to assess the hypoxic state of individual tumours in vivo with the high resolution afforded by MRI while simultaneously providing therapeutic effect. This also allows for a follow up of the treatment in real time.

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Printable Mediated Glucose Biosensor Development for Wearable Devices

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A multiparametric, non-invasive and reagentless sensing strategy for diabetic monitoring is proposed based on a bespoke graphite ink "writable" formulation (including biocompatible binders and modifiers, Gink) (Fig. 1) as conductive layer for biocatalyst immobilisation within an epidermal patch. This enables encapsulation of the heterocyclic quinoid species 1,10-phenanthroline-5,6-dione [1] which acts as a proton and electron acceptor for $FADH_2$ cofactor regeneration of glucose oxidase. Optimisation and characterisation of the Gink on glassy carbon electrodes involved electrochemical, surface and optical investigations. Multiple methods of PD immobilisation have been attempted to date and their performance evaluated, including: (i) Gink doping at various loadings (ii) electrodeposition of a PD poly/oligomer film on the underlying GInk and (iii) enzymatic PD polymerisation in the presence of glucose oxidase, aided by substrate addition and subsequent hydrogen peroxide production. A "layer by layer" enzyme entrapment method was employed for glucose oxidase entrapment and the electrocatalytic response upon glucose additions was followed using cyclic voltammetry and differential pulse voltammetry (DPV) resulting in calibration curves over the range 0.1-2.0 mM glucose. The optimum method (iii) was transferred as a proof of principle to a carbon cloth electrode (Fig. 2) and successful glucose response was obtained as a result of monitoring the electrocatalytic cathodic DPV process.

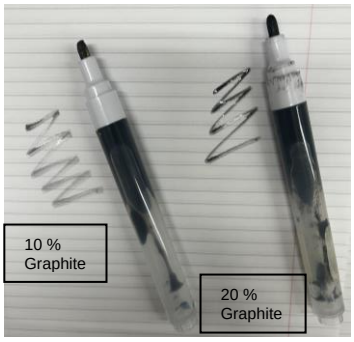

Figure 2: GInk in refillable pens

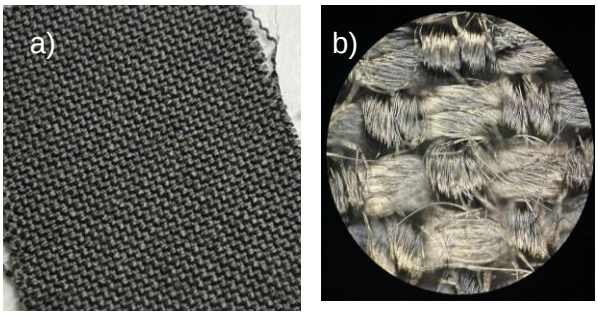

Figure 1: a) Carbon cloth on bench b) Carbon cloth under reflectance microscope x10 mag

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Characterisation of a Polymer-Enzyme Composite Biosensor for Brain Extracellular Glucose

P22

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The aim of this project was to develop and characterise a polymer/enzyme composite biosensor for monitoring brain extracellular glucose[1]. Glucose is an important neurochemical acting as the primary source of energy for the brain and is associated with several essential functions including cell signalling process and memory formation. Additionally, abnormal levels of glucose have been linked to neurological diseases such as Alzheimer's disease[2].

The composite biosensor was constructed by surface modification of a Pt/Ir (90/10) disc electrode as follows: a layer of poly-*ortho*-phenylenediamine (P*o*-PD) was electrodeposited onto the electrodes' surface, followed by a layer of Styrene (Sty), then 15 sequential layers of glucose oxidase (GOx), and glutaraldehyde (GA), were then applied consecutively, with a 4-minute drying time between each complete coating sequence. The resulting Pt-*PoPD*-Sty-$(GOx\text{-}GA)_{15}$ biosensor was then allowed to dry overnight before use. In our poster presentation, we will report characterisation data for sensitivity, selectivity, interference rejection, etc., and compare this data with a previously reported and validated classical first-generation glucose biosensor[3].

References:

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Development of a Redox-Neutral Wittig Reaction Catalysed by Phosphorus

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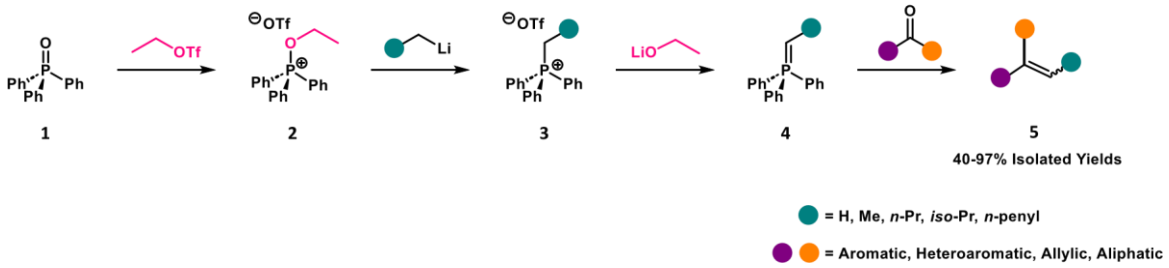
The Wittig reaction remains the cornerstone of olefin synthesis enjoying broad applicability and tolerating a diverse range of functionalities.[1] This reaction generates stoichiometric phosphine oxide waste which is expensive to purify and atom uneconomical.[2]

The ACS green chemistry pharmaceutical roundtable named the Wittig reaction 'one of the top ten key green research areas' sparking interest in developing methodologies for phosphorus catalysed Wittig reactions. There are already established redox-shuttled,[4-6] electrochemical,[7] and microwave assisted[8] catalytic Wittig reactions. However these approaches do require stoichiometric base and reductant additions diminishing their overall atom economy. An alternative 'inverse reactivity' approach developed in this project. Using alkyl triflate and alkyllithium reagents, the basis for a new catalytic Wittig reaction has been developed as shown in **Scheme 1.**



Scheme 1: Wittig reaction employing triphenylphosphine oxide **1** as starting material.

With this method triphenylphosphine oxide **1** is alkylated by ethyl triflate to generate ethoxyphosphonium triflate **2**. Displacement of the ethoxy leaving group by alkyllithium reagents forms quaternary phosphonium salts **3** and ethoxide base. The *in situ* generated base deprotonates **3** affording non-stabilised *P*-ylides **4**. Reaction with aldehydes and ketones yields alkenes **5** in moderate to good yields (40-97%), triphenylphosphine oxide **1** starting material and simple lithium triflate and ethanol waste products.

References:

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For what's next

Design, synthesis and screening of novel prenylated chalcones as optimised anti-cancer agents

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The anti-cancer potential of simple chalcones has been an intense area of research for some years, which has allowed structure-activity relationships to be well defined. Although many such examples display cytotoxic properties, important predictors of activity are the presence and position of hydroxyl and methoxy groups. More complex chalcones are those incorporating branched alkyl substituents, borne either on carbon or oxygen atoms. An important example is the liquorice metabolite, licochalcone A (LA), which, alongside related prenylated chalcones are increasingly seen as valuable lead compounds, due to their interesting anti-cancer activities. For example, LA exhibits phytoestrogenic properties, and is capable of modulating bcl-2 protein expression. It has been shown to decrease cell proliferation and to increase ROS production, and via regulation of E-cadherin and vimentin, may reduce cell migration and invasion. The drug has shown potential benefit in combination with a range of established chemotherapeutics for diverse cancer cell lineages, including glioma. To prepare novel chalcones derived from LA, we reacted O-prenylated aldehydes with different acetophenone derivatives substituted at 3’ and 4’ positions of the phenyl ring. We also varied the phenyl ring by replacement with heteroaromatics. Rearrangement of the novel O-prenylated chalcones via 3,3-sigmatropic reaction resulted in the novel licochalcone A analogues.

This poster presents the synthetic methods developed to prepare the aldehyde and ketone precursors of a family of LA and prenylated chalcone analogues, and to describe the reaction conditions necessary for the condensation of these precursors. Requisite prenylated aldehydes were condensed with either monocyclic acetophenone derivatives or various heterocycles (including chromans and chromanones), with a key subsequent reaction being Claisen rearrangement of the substituted alkenyls. The resultant products represent novel heteroaryl systems, and we further show the results of preliminary cytotoxicity testing of our compounds on brain cancer cell lines.

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* Presenting author. E-mail address: mounahindlaiche22@rcsi.ie (Mouna Hind Laiche).

Desulfurative Fluorination of Alkyl Phenyl Sulfides via Bromonium Catalysis

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Fluorine-containing compounds make up 20% of pharmaceuticals and 50% of agrochemicals on the market. Benefits of fluorine in pharmaceuticals includes modulating pharmacokinetic and pharmacodynamic properties, and use of ^{18}F radioisotope in diagnostics and drug development. [1]

Despite the prevalence of fluorine in pharmaceuticals, synthetic methodologies for its introduction onto sp^3 carbons often suffer from harsh reaction conditions, poor selectivity, and a necessity for specialised transition metal catalysts. Following from previous research in the group developing fast and mild desulfurative chloro- and bromination reactions,[2,3] we sought to generate a suitable fluorination variant for the late-stage incorporation of fluorine.

Herein, we describe a novel reaction for the mild, fast and selective introduction of fluorine in high yields. A sacrificial thioether group is introduced that can be replaced by fluorine via a tandem thioether oxidation/Pummerer fragmentation pathway (Fig. 1.).

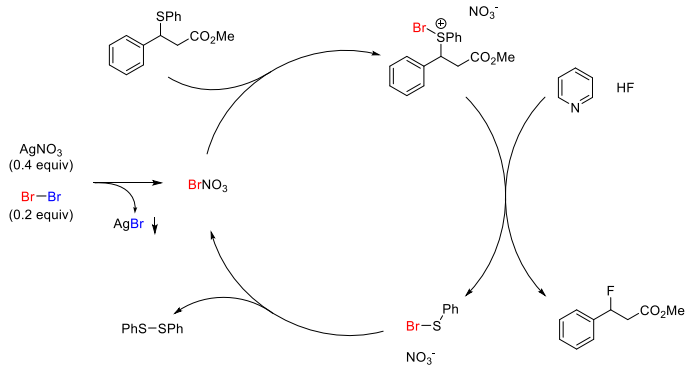

Figure 1. Catalytic Bromonium Mediated Fluorinative Pummerer Fragmentation

The reaction is enabled by sub-stochiometric amounts of Br_2 (0.2 equiv) and $AgNO_3$ (0.4 equiv) and use excess of (HF-Pyridine) as the source of fluorine. Typically, full conversion to the fluoride is achieved in minutes. We propose this transformation being enabled by an in situ generated $BrNO_3$ which upon reaction with sulfides installs a catalytic cycle.

Studies have revealed extensive functional group compatibility, with compounds bearing electron rich and deficient aromatic groups, esters, ketones, nitriles, mesylates, silyl ethers, nitro, amides, carboxylic acids, alcohols, triazoles and amidines all proceeding to the corresponding fluorinated compounds in good to excellent yields (Fig. 2.)

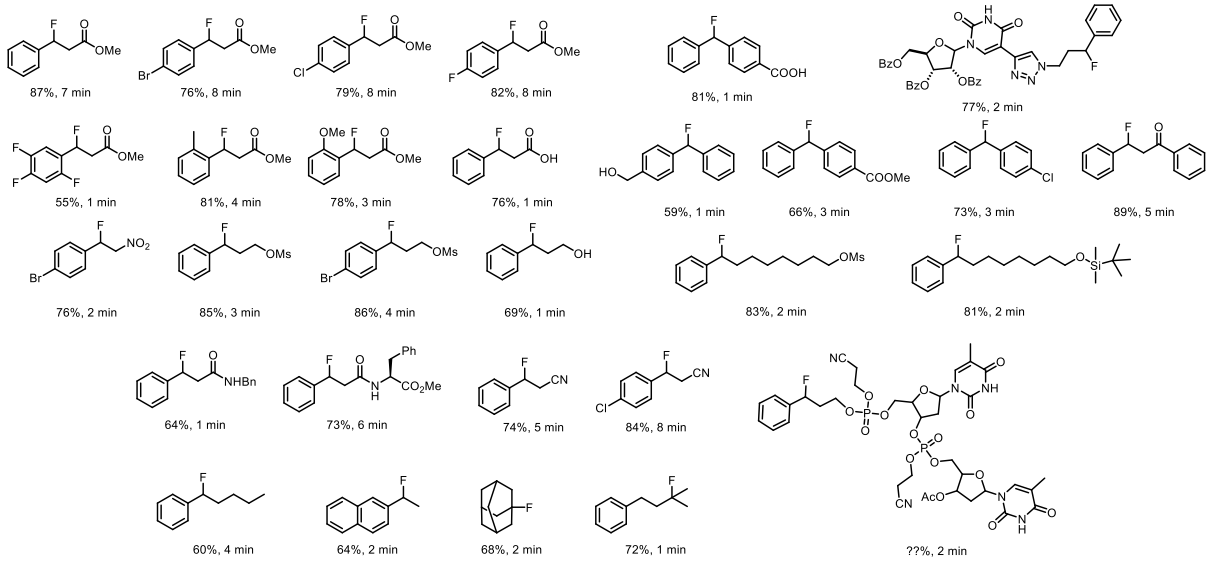

Figure 2 Substrate Scope

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Investigation of the protein corona of gold nanoparticles as a possible biomarker for glycan based diagnostics

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In nanomedicine gold nanoparticles are used due to their established and reproducible synthesis, tunable sizes, tailorable optoelectronic properties, and the possibility to functionalise their surface with a wide range of ligands, polymers, and biomolecules. [1]

When a nanoparticle is exposed to a biological fluid, a layer of biomolecules associates with the nanoparticle forming around it the so called protein corona. The protein corona composition is strongly related to the nanoparticle's intrinsic properties, like size, surface charge, material, shape, etc., and it determines the biological identity of the nanoparticle. [2]

Glycosylation is a post-translation modification that occurs to all proteins where glycans are enzymatically bound to the protein backbone with a specific order and composition. It is generally recognised that under chronic diseases, proteins can carry altered glycan structures. Therefore, being able to detect these changes could be particularly useful in early disease discovery. However, glycans are not easy to detect and characterise and require a dedicated infrastructure. [3]

In this study, we evaluate whether glycan structural changes can be characterised using gold nanoparticles with different shapes and the protein corona formed in different conditions around these nanoparticles using several physiochemical characterisation techniques, with a focus on the changes in their optical and localized plasmonic properties.

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Platinum black and miniaturised electrodes for neurochemical monitoring

K. McNamee, Prof J.P. Lowry

This body of work is focused on miniaturisation of a biosensor to facilitate multiplexing while still maintaining a robust and reliable signal. The aim of my research project is to develop a biosensor to enable the real-time neurochemical monitoring of GABA *in-vivo.* To achieve this a dual enzyme system has to be used as GABase requires a co-factor α-ketoglutarate, luckily this a product of the reaction between glutamate and glutamate oxidase. This allows the monitoring of GABA to be achieved using a sensor system. One monitoring GABA and glutamate currents the other monitoring glutamate currents and the GABA current can be found via subtraction.

To facilitate, using multiple sensors while minimising tissue damage following implantation it is necessary to make the sensor as small as possible. This causes no issues when all currents are normalised with respect to surface area, however the overall magnitude of the signal dramatically increases leaving the system more susceptible to noise and interference resulting in a non-reliable signal. In an attempt to overcome this issue it was decided to increase the surface area of the electrodes using platinum black in hopes this can increase the overall size of the signals obtained from smaller biosensors by:

1) Increasing the number of sites available for H_2O_2 oxidation,
2) Provide more sites for enzyme immobilisation.

The first step will to be ensure the deposits are stable and replicable between batches and that there is a sufficient increase in H_2O_2 sensitivity and therefore area on 127-µm electrodes as this is what's been typically employed in the lab previously. Then the platinum black deposits will be used on the glutamate sensor which has been published by the group[1] to see if platinum black can increase the sensitivity. Then the platinum black glutamate biosensors will be tested to ensure this increased surface area maintained sufficient ability to provide a signal free from endogenous electroactive species. Once the 125-µm sensors have been shown to provide an increased signal magnitude and maintained selectivity 75-µm and 50-µm sensors will have Pt black deposited to hopefully provide a signal large enough to provide reliable *in-vivo* monitoring.

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Nickel boride/transition metal dichalcogenides as potential bifunctional electrocatalysts for water splitting

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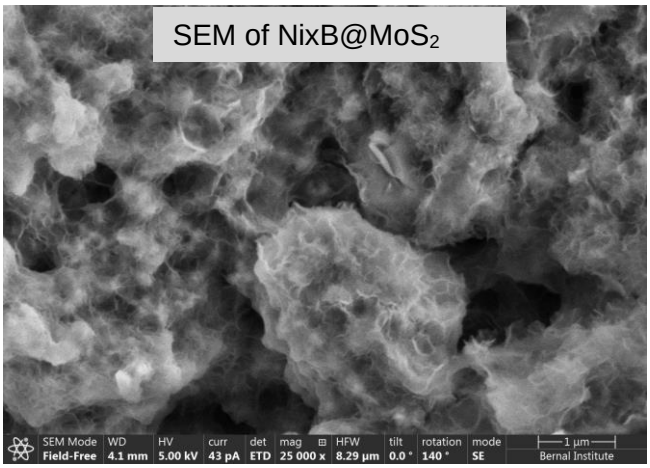
Here we present new sustainable, low cost electrocatalytic materials for the Hydrogen evolution reaction (HER) and Oxygen Evolution reaction (OER). The research involves the preparation of transition metal dichalcogenides (TMD) heterostructures to include MoS_2, WS_2, and $MoSe_2$ combined with transition metal borides (Ni_xB). Using a simple wet-chemical synthesis process, TMD heterostructures were synthesised including MoS_2, $Ni_xB@MoS_2$, $Fe\text{-}Ni_xB@MoS_2$, $Co\text{-}Ni_xB@MoS_2$ together with testing of other bulk TMD material combinations (WS_2, $MoSe_2$) and hydrothermally synthesised MoS_2. Initial HER and OER experiments were performed at a glassy carbon electrode (GCE) with challenges of bubble formation and associated signal noise. The use of 3D and 2D nickel foam porous substrates alleviated this issue, providing a high surface to volume ratio for catalyst immobilisation using a number of approaches to include dipping, painting, hydrothermal preparation and electrochemical deposition. Materials were all tested under alkaline conditions and their stability examined by monitoring the current over periods of time. Relative to Pt HER (standard material, E_{onset} = -0.01 V vs RHE), the MoS_2 catalyst resulted in an onset potential (E / V vs RHE) of -0.332 V while $Ni_xB@MoS_2$ resulted in a value of -0.358 V, indicating higher overpotential for the HER. In the case of the latter, the potential at current density of 10 mA/cm^2 was however lower indicating greater efficiency. The $Fe\text{-}Ni_xB@MoS_2$ material resulted in E_{onset} of -0.295 V vs RHE with potential at 10 mA/cm^2 of -0.4246 V and Tafel slope -105 mV/decade, all of which indicated superior HER performance relative to other materials under study. Parallel OER investigations were carried out and materials which were combined with MoS_2 i.e. $Ni_xB@MoS_2$, $Fe\text{-}Ni_xB@MoS_2$, were found to be the most promising candidates as bifunctional catalytic materials with E_{onset} of 1.58 V and 1.51 vs RHE and E(V) at 10 mA/cm^2 of 1.67 V and 1.6 V respectively.



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Dual Delivery of Anti-Cancer Drugs using Metal-Organic Framework

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Metal-Organic Frameworks (MOFs) have the potential to offset some of the terrible side effects caused by the drugs currently used in cancer treatment. MOFs have high porosity, low cytotoxicity, good biocompatibility, biodegradability, and target-specific behavior, encapsulating drugs and subsequently releasing them at tumor sites. MOFs allow for a slower release of the drugs, preventing the burst effect caused by immediate release of the drug [1]. Although the potential of MOFs as drug carriers has been well established, their use in combinatorial treatments that involve more than one drugs has been less investigated. Dual drug delivery would improve the potency of the anti-cancer treatment because of the synergistic effect of the two drugs. Dual drug delivery can also help to overcome the multidrug resistance effect that comes from cancer cells becoming resistant to anti-cancer drugs. [1]

With the above in mind, we decided to explore the potential of MOFs as multiple drug carriers. For this purpose, NUIG4 was used (Fig. 1). NUIG4 holds the record in doxorubicin (DOX) uptake, it is water stable and biocompatible, and protects the healthy cells from the drug cytotoxicity. [1]

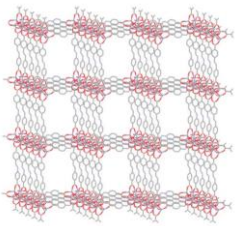

Figure 1: Representation of the crystal structure of NUIG4.

Herein, the capacity of NUIG4 to deliver dox or mitoxantrone (MIT) and 5-fluorouracil (5-FU) is reported. Each anti-cancer drug that are used in this project have a different mechanism of action; this can help to overcome multidrug resistance. 5-fluorouracil intercepts the replication of the cancer cells genetic material, due to the cancer cells mistaking 5-fluorouracil for uracil [2], while doxorubicin hydrochloride intercepts the replication process of the cancer cells by DNA intercalation, it slots itself between the base pairs of DNA [3]. Mitoxantrone is a synthetic anti-cancer drug which is similar in structure to anthracycline drugs, such as doxorubicin hydrochloride. It has a similar mechanism of action to that of doxorubicin hydrochloride [4]. The initial results suggest the successful encapsulation of DOX/ MIT and 5-FU, and a controlled release of the drugs, as a result of the large pore size and subsequent large internal surface area.

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Observing bioorthogonal macrocyclization in live cell nuclear membranes using on/on fluorescence lifetime microscopy

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Bioorthogonal fluorescence imaging is an effective way of monitoring dynamic events in sub-cellular compartments in a non-destructive manner. The Sondheimer diyne allows for two sequential 1,3-dipolar cycloadditions under mild conditions without the need for a catalyst.[1] Previous work from the O'Shea research group has shown that this diyne can be used for bioorthogonal imaging in live cells.[2] To expand on these initial findings, the bis-azide substituted BF_2-azadipyrromethene **1** was selected as an attractive candidate for bioorthogonal fluorescence imaging as it would emit in the advantageous near infrared spectral region and has bis-azide functionality allowing for two cycloaddition reactions (Figure). The synthesis of **1** was achieved in 10 steps starting from butan-1,4-diol and 2-bromo-4'-methoxyacetophenone. Photophysical characterization of **1** showed an emission λ_{max} at 677 nm with quantum yield of 0.49 in methanol. The reaction of **1** with Sondheimer diyne gave a mixture of *cis* and *trans* macrocyclization products **2** in excellent yield under mild room temperature conditions (Figure). Preliminary live cell imaging showed that **1** localizes to lipophilic membrane regions and investigations are ongoing to determine its ability to participate in bioorthogonal double click [3+2] cycloadditions in live cells.

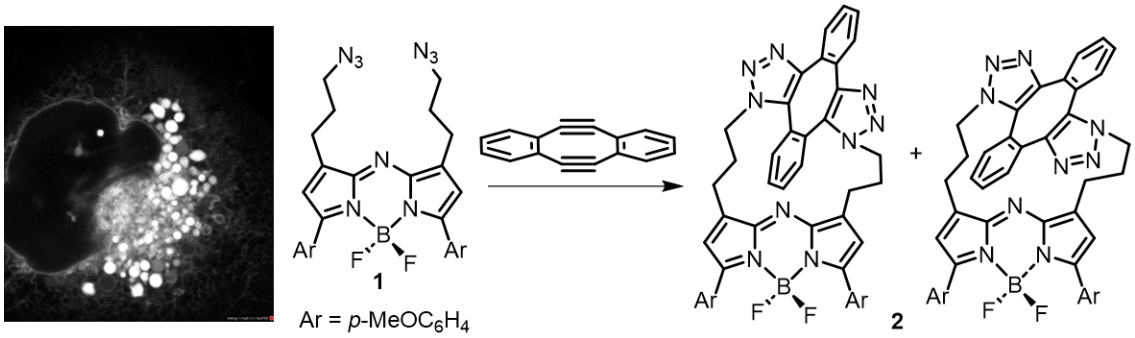

*Figure 1 – Schematic of bioorthogonal macrocyclization reaction of BF_2-azadipyrromethene fluorophore **1** with Sondheimer diyne. Confocal microscopy image of **1** in MDA MB 231 cells.*

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Asymmetric Synthesis of α-Aryl Stereocentres in Dihydroquinolinones *via* DAAA and DAP

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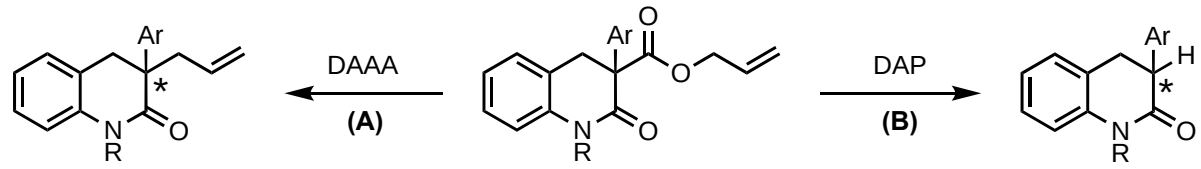
Heterocycles constitute a significant portion of therapeutic agents in medicinal chemistry and are a prevalent motif in natural products.[1] Many biologically important molecules contain α-aryl stereocentres. Pd-catalysed decarboxylative asymmetric transformations of α-aryl β-amido/keto allyl esters is an effective route to install these centres. The allylic group is a well-explored functional handle that has many applications in the synthesis of a wide range of structures. Our group has previously applied this decarboxylative catalysis to a range of substrates possessing α-aryl motifs.[2]

This project explores the synthesis of nitrogen-containing heterocycles via decarboxylative asymmetric transformations. The synthesis of α-allyl, α-aryl 3,4- dihydroquinolinones via decarboxylative asymmetric allylic alkylation (DAAA) will be described, with a range of substrates transformed to the desired product in high conversions and moderate enantioselectivities **(A)**. The synthesis of α-aryl 3,4-dihyroquinolinones via decarboxylative asymmetric protonation (DAP) will also be outlined, with good yields and excellent enantioselectivities **(B)**.



up to 98% conversion
up to 68% *ee*

R = Boc, Bz, Bn, Me

up to 95% yield
up to 90% *ee*

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High-Valent Iron Halide Oxidants for Hydrocarbon Oxidation

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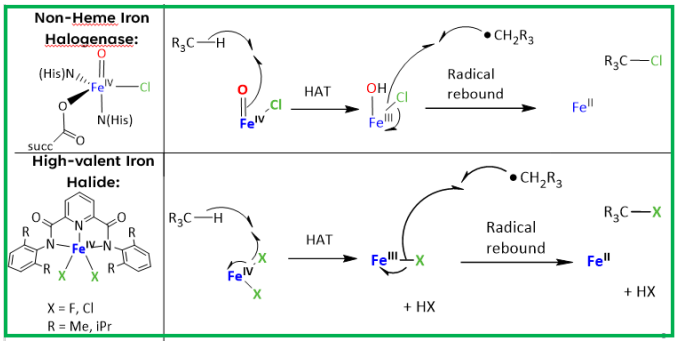
Mild oxidative functionalisation of saturated hydrocarbons has remained a challenge in the chemical industry for many years because of their inherently strong C-H bonds.[1] Therefore, mild and selective methods to convert hydrocarbons into more useful, functionalised products such as halogenated organic products are highly sought after from both synthetic and environmental perspectives. Currently, fluorinated and chlorinated organic products have many applications in the chemical and pharmaceutical industries. It is estimated that 30 % drug molecules in clinical trials are halogenated.[2-4] Current halogenation techniques involve the use of harsh reaction conditions (high temperature and pressure), and the use of corrosive and toxic reagents, such as elemental halogens and hydrogen halides. These reactions are non-selective and can generate undesirable waste products.[2, 5]

Inspiration for the functionalisation of inert hydrocarbons can be taken from naturally occurring metalloenzymes. Biological non-heme iron halogenase enzymes perform selective chlorination of hydrocarbons via a high-valent iron(IV)-oxo reactive intermediate.[6] Efforts have been made to synthesise catalysts that mimic the reactivity of halogenases, with a high-valent metal-oxo moiety as the active oxidant.[7-8] Unfortunately, these systems are often unable to activate inert hydrocarbons and have poor reaction rates due to the properties of the metal-oxo active species.[9] We aim to synthesise high-valent iron dihalide oxidants to achieve oxidative halogenation of hydrocarbons. We have synthesised three novel iron(III) dihalide complexes and aim to chemically oxidise these complexes to their analogous high-valent iron(IV) dihalide derivatives. It is anticipated that these high valent complexes will react with hydrocarbon molecules, with a halide ligand performing both the hydrogen atom transfer (HAT) and the radical rebound step. Finally, we will investigate the reactivity of the high valent complexes towards hydrocarbon substrates with a variety of C-H bond strengths.



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Glutathione Sensor Development with the aid of Electrosynthesised Nanogold

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Reactive oxygen species (ROS) are highly reactive molecules that may contain unpaired electrons. At low levels, ROS are biologically important as they act as signalling molecules and defend against infections. At high levels they can result in oxidative stress that can cause damage to biomolecules such as enzymes, amino acids, lipids, and DNA. To combat high levels of ROS, the body has an antioxidant system comprised of enzymatic and non-enzymatic antioxidants. There are key molecules that play a part in this antioxidant system and a change in the levels of these molecules can indicate the progression of a neurodegenerative disease, dementia and certain cancers [1]. The brain is particularly vulnerable to oxidative damage and reactive oxygen species can contribute to the development of disease. One of the molecules associated with a non-enzymatic antioxidant system is glutathione, as it acts a scavenger of free radicals to balance out the levels of ROS in the body. This molecule exists in the body in both reduced (GSH) and oxidised (GSSG) form with a ratio of 500:1 respectively. However, a change in this ratio could occur due to high levels of free radicals which indicates the development of a neurodegenerative disease [2]. This research focuses on using gold nanoscale materials (electrodeposited and chemically synthesised) as electrocatalysts which enable sensitive and rapid electroanalysis of glutathione. Optimal electrodeposition conditions resulted in a GSH oxidation signal which was distinct from the gold oxide anodic response, reflecting the formation of GSSG, and exploiting the high surface to volume ratio AuNP surface. We also examine the use of carbon nano onions (CNOs) which are concentric multilayered fullerenes consisting of graphitic shells [4], as an underlying conducting support for the AuNP formation. Work to date has included optimisation of the drop casting immobilisation method for suspensions of CNOs and promising data has been generated using differential pulse voltammetry which will be extended with respect to gold electrodeposition investigations.

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Ultrasensitive Detection of Sulfamerazine with CeO_2 mixed Spherical Spinel $ZnMn_2O_4$ combined with WS_2 Sheets

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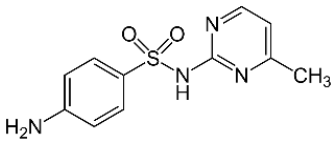
Antibiotics are extensively used in various industries such as veterinary medicine, agriculture, aquaculture, beekeeping, and animal husbandry to promote growth. Due to their resistance to degradation, antibiotics can seep into water systems, including surface and groundwater, through industrial wastewater. This contamination leads to disruptions in microbial populations and contributes to increased bacterial resistance [1]. Sulfonamides, the second most widely used antibiotics globally, are commonly detected in the environment, with sulfamerazine (SRZ) being a typical example. The development of highly sensitive electrochemical sensors is crucial for accurately detecting and monitoring pharmaceutical drugs in water systems due to their significant pollution and potential impact on the ecosystem [2].



sulfamerazine (SRZ)

Spinel nanomaterials have gained significant attention in recent years owing to their unique properties and promising applications, such as high-density data storage, catalysts, gas sensors, rechargeable lithium batteries, information storage systems, magnetic bulk cores, magnetic fluids, microwave absorbers and medical diagnostics and therapy, etc. Spinels can be represented as AB_2O_4, to give a cubic close-packed lattice arrangement, where A and B represent the cations positioned in the tetrahedral and octahedral sites [3]. By tailoring the synthetic route, well-defined crystal lattice structure and chemical composition can be obtained, leading to enhanced/excellent physical and chemical properties.

This study presents a simple, cost-effective, highly sensitive, and reliable sensor for the detection of sulfamerazine (SRZ) using an electrochemical method. The sensor was fabricated by modifying a glassy carbon electrode (GCE) with CeO_2-mixed spherical spinel $ZnMn_2O_4$ (ZMO) combined with WS_2 sheets through a wet-chemical synthesis approach.

The modified GCE showed an oxidation peak for sulfamerazine analytes at 0.8 V vs Ag/AgCl. It also demonstrated limited interference effects on SRZ detection, along with good selectivity, stability, reproducibility. The developed electrochemical sensor was successfully used to detect SRZ in water samples, showing acceptable recovery rates in the range of 98.7%. This work paves the way to design a high-performance sensing material for the detection of antibiotics and other eco-hazardous pharmaceutical drugs.

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Rigid Hydrocarbon Isosteres as Linkers in Porphyrin Dyads for Sensing Application

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Traditionally, multi-porphyrin arrays are networks of two or more porphyrins connected by rigid linkers like benzene or alkyne groups, resulting in systems with increased electron delocalization. The unique electronic properties of these compounds have led to their application in a variety of materials from molecular wires to light harvesting molecules [1], [2]. However, as these arrays typically consist of conjugated linkers, modulation of the material properties of the arrays has been limited.

Rigid hydrocarbons like bicyclo[1.1.1]pentane (BCP) and cubane have recently gained interest as isosteres for alkynes and benzene units respectively (Figure 1). Isosteres are compounds which act as drop- in replacements for moieties within a molecule, modifying the chemical properties while preserving the physical structure. The replacement of conjugated linkers with non-conjugated linkers, BCP or cubane, in multi-porphyrin arrays maintains rigid connectivity while decreasing conjugation between individual porphyrins. This modification allows for selective modulation of the multi-porphyrin arrays' chemical properties, resulting in the potential for unique optical, electronic, and sensing applications.

Here we present a library of BCP and cubane based linkers for symmetric and non-symmetric porphyrin dyads with different linker lengths and controlled connectivity (Figure 1) [3]. The structure, properties, and sensing abilities of both BCP and cubane-linked porphyrin dyads will be discussed [4].

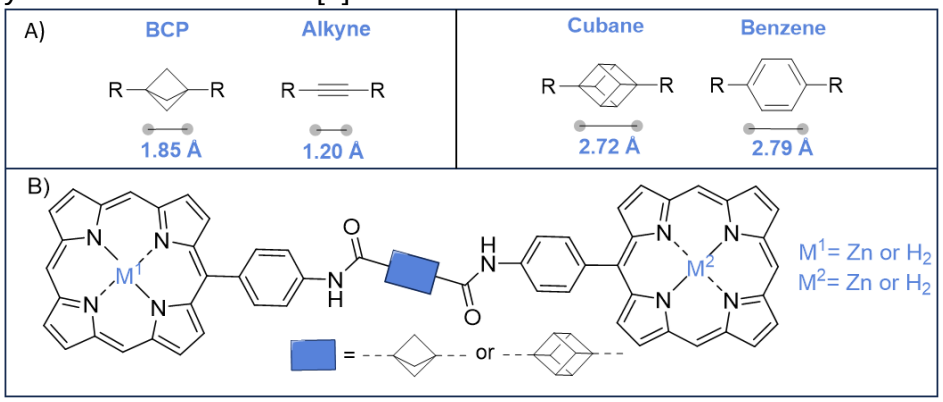

Figure 1A) Examples of rigid aliphatic hydrocarbons as isosteres. B) Model of symmetric and non-symmetric porphyrin dyads synthesized.

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Electrochemical Evaluation of FeCo Oxide and Ag/FeCo Oxide Nanocomposites Derived from Prussian Blue Analogues for Oxygen Evolution

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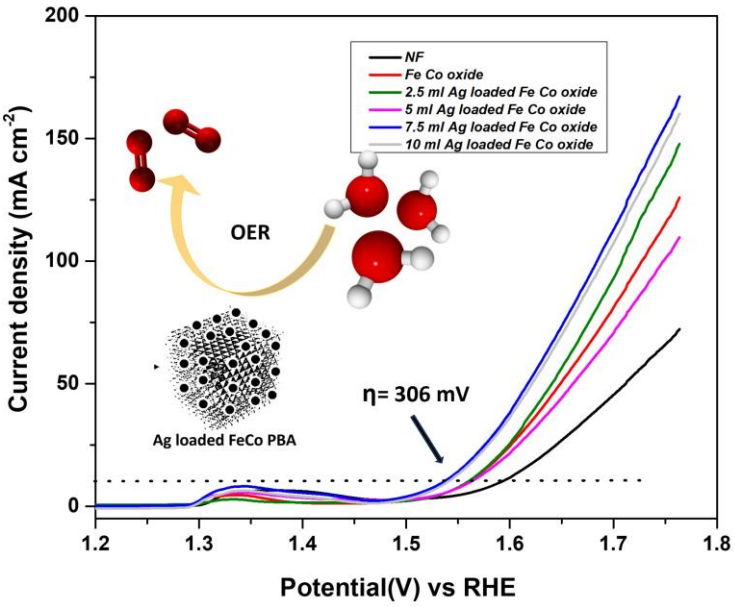

Metal-organic frameworks (MOFs), including Prussian blue and its analogues (PB/PBA), are promising materials for oxygen evolution reactions (OER) due to their high surface area, tunable compositions, and well-defined porous structures[1, 2]. In this study, the synthesis of silver-loaded spinel metal oxides derived from PBAs with variable Ag compositions demonstrate promising potential for OER. The thermal conversion of FeCo-based PBAs into a unique iron-cobalt oxide (FeCo oxide) structure, is characterized by a rough, permeable texture with interconnected granular particles and surface voids. An innovative in-situ generation of silver nanoparticles through wet impregnation with silver nitrate followed by annealing was employed to enhance the structural features. The synthesized Ag/FeCo oxide was extensively characterized using techniques such as XRD, FTIR, TEM, and XPS. The X-ray diffraction (XRD) analysis of the synthesized Ag/FeCo oxide catalysts , exhibited diffraction peaks at 38.2°, 44.3°, 64.6°, and 77.6°, corresponding to Ag(111), Ag(200), Ag(220), and Ag(331), respectively, confirming the successful loading of Ag onto the CoFe oxide framework[3]. The catalyst exhibited exceptional OER activity, attributed to its extensive surface area and the efficient electron transfer between Ag nanoparticles and FeCo oxide. The optimization of Ag-loading facilitates the reduction of charge-transfer resistance within the spinel structure of FeCo oxide, consequently leading to enhanced electrocatalytic activity for OER. The as-synthesized Ag loaded FeCo oxide exhibits good OER activity with a remarkably low overpotential of 306 mV at 10 mA cm^{-2} and sustained stability for at least 12 hours of continuous operation in an alkaline solution. Additionally, these catalysts showed a high level of recyclability in the presence of an external magnetic field, which makes them suitable for practical applications. These findings emphasise the possibilities of altering electrocatalytic activities through the control of metal composition in Ag-loaded metal oxides derived from PBA for potential applications in various catalysis and green chemistry areas.

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Utilisation of Surface-Modified Transition Metal Dichalcogenides as Unconventional Antimicrobial Agents

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The United Nations has identified the rise in antimicrobial resistance as one of the largest emerging threats to the health sector [1]. The production of new antibiotics is struggling to meet demand as bacterial species continue to develop resistances to common antibacterial treatments.

Two-Dimensional Transition Metal Dichalcogenides (2D-TMDs) have recently come into focus due to their wide range of possible applications in electrochemical sensing, water splitting and drug delivery. Their nanosheet structure is very similar to that of graphene, which has demonstrated antimicrobial properties [2], the antimicrobial potential of different 2D-TMDs is now being investigated.

The nanosheets allow for a knife-like interaction with bacterial cellular membranes, inhibiting bacterial growth. Molybdenum Disulfide (MoS2) showed particular promise for bacterial growth inhibition. This inhibition was optimised by reducing metal oxides (CuO and CoO) onto the surface of the material. This method was previously reported to improve the electrocatalytic ability of MoS2 [3]. The reduction process involved refluxing at 85 °C and it was found that this led to an increase in the number of small single layer sheets (rMoS2), increasing the antimicrobial activity of the nanosheets. These surface modifications allowed for increased bacterial inhibition of E. Coli strain MG1655. It was found that the inhibition of bacteria increased as bacterial and material concentration increased. The effect of multiple doses of material was investigated and it was found that 2 doses of CuO and CoO decorated could completely inhibit the growth of bacteria for 24 hours.

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Continuous flow synthesis of Black Hole Quenchers

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Black Hole Quenchers (BHQs) are important fluorescence quenchers used in Reverse Transcription Polymerase Chain Reaction (RT-PCR) tests[1]. In RT-PCT testing, BHQs are used to quench the fluorescence signal of a fluorophore until amplification has occurred. The availability of high quality and low-cost test reagents, such as BHQs, is essential for the economical production of testing systems for viral infections.
Current BHQ synthetic strategies employ exothermic batch processes and hazardous diazonium species[2]. Highly exothermic batch reactions can generate hot spots, and can result in runaway reactions, while unstable diazonium species can generate large volumes of nitrogen gas upon decomposition and can be hazardous to use in large batch reactions. The use of continuous flow processes in BHQ synthesis offers several potential benefits over batch reactors including improved heat-mass transfer, reproducibility, scale-up, multistep synthesis and improved safety profile[3].

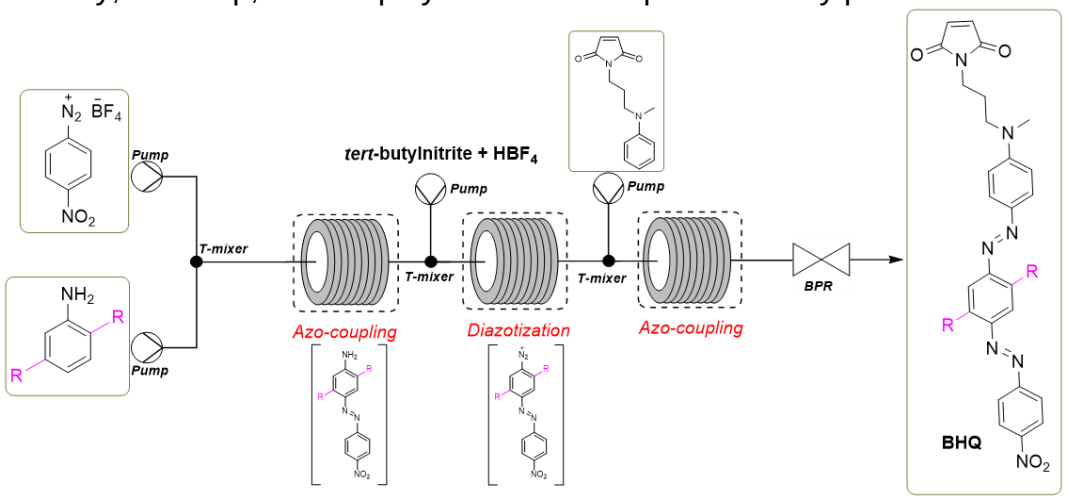

Figure 1: Proposed multistep continuous flow schematic for BHQ synthesis.

The ultimate goal of our work with BHQs is to generate a multistep continuous flow synthesis as exemplified in simple terms in Figure 1. To date, we have completed single step azo-couplings in continuous flow and generated a number of known and novel BHQs using batch and continuous systems.

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Structurally Dependent DNA Disruption of Phthalocyanine Aggregates

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Phthalocyanines are promising photosensitisers for the light-activated anti-cancer therapies: photodynamic therapy (PDT) and photothermal therapy (PTT).[1] They possess advantages over other drugs due to their modifiable photochemical properties, strong absorbance in the biological window and low absorbance at the peak of the solar spectrum but can be hampered by solubility and stereopurity challenges.[2] A library of regioregular pegylated phthalocyanines that are monomeric in DMSO but form soluble aggregates in water have been synthesised.[3] In DMSO, the phthalocyanine is highly emissive which could allow singlet oxygen generation for PDT. In water, there is quenching of luminescence and upon photo-excitation, non-radiative relaxation causes heat release for PTT.

The interaction between this phthalocyanine system and DNA systems has been investigated using UV-vis, emission and CD spectroscopy. The phthalocyanine aggregates have been found to be disrupted by G-rich nucleic acids including GpG, $(GG)_{10}$, poly(G) and G-quadruplex DNA in comparison to the interaction with natural double stranded DNA which has shown limited aggregate disruption. For the extended poly(G), significant time-dependent binding is observed which indicates that changes in local conformation over time allows further monomer accommodation. An increase in the rate of aggregate disruption in the presence of KCl was attributed to the increase in formation of guanine tetrads. $(GT)_{10}$ was found to be particularly effective at disrupting the aggregation which could be due to the formation of mosaic structures that accommodate the phthalocyanine complexes. These comparisons show the importance of local DNA conformation to phthalocyanine disaggregation which will impact the activity of the phthalocyanine intracellularly.

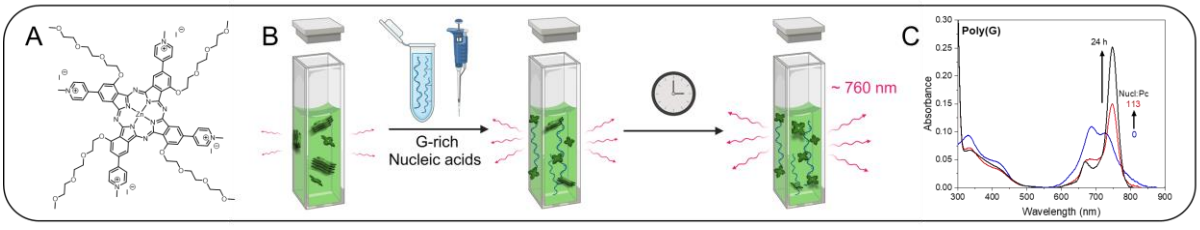

Figure 1: (A) Structure of zinc phthalocyanine. (B) Schematic of addition of DNA to aqueous phthalocyanine solution. (C) Change in absorption spectrum of zinc phthalocyanine (blue) upon addition of poly(G) (red) and following 24 hours (black).

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Room Temperature Modification of Carbon Cloth for Water Splitting

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The energy production sector has faced many challenges, especially regarding the environmental impacts caused using fossil fuels. Renewable hydrogen, generated via electrolysis of water, has emerged as a possible solution to reducing global reliance on fossil fuels as a source of energy. Many emerging catalysts are made using hydrothermal synthesis, demonstrating good water-splitting performance. However, the methods used to make such materials can be time and energy-consuming, while generating a significant quantity of chemical waste, which remain in the environment for long periods. This study focuses on the development of a new environmentally benign, solvent-free, room-temperature synthesis design taking advantage of abundant, low-cost materials.

In the first stage of this study, a room temperature deposition of Molybdate (Mo) on the surface of Nickel Foam (NF) was identified. This material resulted in a very good performance in relation to the oxygen evolution reaction (OER). However, NF is an effective catalyst for water splitting, making it challenging to discriminate the effectiveness of immobilised electrocatalysts and the formation of oxides can give false results. To address these issues, in the second phase of the work, carbon cloth (CC) was used as a substrate due to its attractive features of low cost, porosity, and lack of catalytic performance in the absence of modification.

Copper was incorporated on the CC by electrodeposition and further modified by this novel one-pot room temperature synthetic approach. CC presented a significant improvement relative to its bare form. Performance data showed good current density, impressive onset potentials, good Tafel slopes, low impedance, and good stability. Both HER and OER were tested in this study. [1–3]

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Enhancing Pyrazolopyrimidinone Cytotoxicity against Glioblastoma using Cold Atmospheric Plasma (CAP)

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Glioblastoma is a fast-growing and aggressive brain tumour. [1] It is one of the most frequent and the most difficult types of brain tumour to treat. [1] Pyrazolopyrimidinones are fused nitrogen-containing heterocyclic systems and can be found in numerous drugs and drug candidates. Cold atmospheric plasma (CAP) is a type of plasma generated at room temperature and can locally induce reactive oxygen species (ROS) generation in cells and tissues with a high degree of control over both the amount of ROS generated and location. [2]

Previous preliminary work within the group involved the synthesis of a small family of pyrazolopyrimidinones and their evaluation for cytotoxic effects in combination with CAP on a glioblastoma U-251MG cell line. Some pyrazolopyrimidinones showed a prodrug like effect that was activated by low doses of CAP treatment. For example, the IC_{50} values of pyrazolopyrimidinones 9 and 10 against U-251MG cells decreased from around 940 to 62 µM, and 290 to 56 µM, respectively, when combined with 30 s of CAP treatment. [2] The objective of this project is the synthesis and evaluation of a larger family of pyrazolopyrimidinones for cytotoxicity against glioblastoma, alone and in combination with CAP. The work will involve a structure activity relationship (SAR) study and aspects of computational chemistry.

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The Synthesis of Mechanically Interlocking Molecules using the btp [2,6-bis(1,2,3-triazole-4-yl)pyridine] motif.

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The world of mechanically interlocking molecules (MIMs) has gained providence since the 2016 Nobel Prize Awards, for which Stoddart and Sauvage received the prize for their pioneering work on molecular machines. Rotaxanes are becoming a more and more prominent MIM in the world of mechanostereochemistry due to their versatility and their never-ending potential. Rotaxanes comprise a ring and a dumbbell component; these components are noncovalently bonded, but to break these components apart, a covalent bond must be broken. This project intends to synthesise novel btp [2,6-bis(1,2,3-triazole-4-yl)pyridine] rotaxanes with a twist, as the synthesised rotaxanes will include various lanthanide metals., allowing for investigations through UV visible titrations and confocal microscopy. Previously, the Gunnlaugsson Group have successfully synthesised btp macrocycles and catenanes so that this project will be building on the foundations already laid. A key element to this project is the use of Scanning Electron Microscopy along with Atomic Force Microscopy to view the topology and the morphology of our btp ligands and pseudorotaxanes. Varying our solvents for drop-casting allows for different morphologies and structures to be formed and viewed using microscopy techniques. The work being presented will focus mostly on the results to date but also on the future work and techniques which will need to be implemented to gain a wider landscape of our intended molecules so they can be utilised in day-to-day life. This project aims to produce and create novel interlocking molecule materials for use within the electronic, imaging, and magnetic industries whilst also aiming to utilise these structures in the formation of 'all organic-based redox-active materials for use in batteries.

Host-Guest Chemistry of Napthalene Diimide based Macrocycles.

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School of Chemistry, Trinity College Dublin, Dublin 2, Ireland.

Macrocyclic structures act as hosts, providing complementarity to guest molecules through various means, including matched size, shape, and the chemical nature of binding sites. These structures have multiple applications, such as chemosensing[1], catalysis[2], and facilitated transport[3]. This work presents macrocycles synthesised using templated self-assembly and probes their host-guest interactions. A novel tetracationic cyclophane was successfully synthesised and characterised. Investigations into the host-guest chemistry of the compound were carried out, using a variety of polycyclic aromatic compounds. Data obtained through single X-ray crystallography, 1H NMR spectroscopy and photophysical measurements infers the successful ingression of these guest molecules. The host-guest binding suggests the motif may be incorporated in larger supramolecular structures.

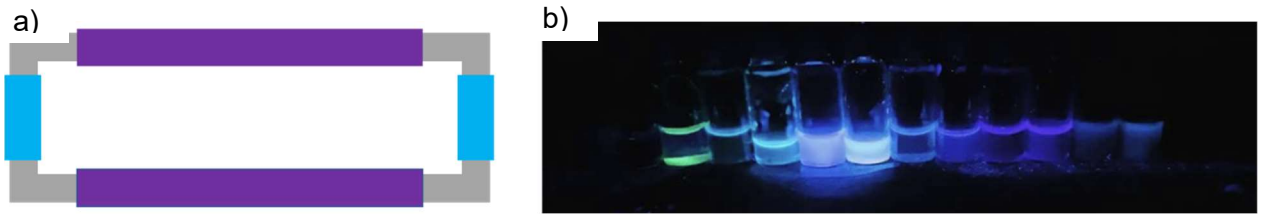

Figure 1. a) Schematic of novel cyclophane b) fluorescence capabilities of the host upon ingression of guest

References:

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Novel Squaratide Based Glycoconjugates (SBG's) to Selectively Target Cancer Cells

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Multivalency (presenting multiple copies of a molecule) has been a concept employed by carbohydrate chemists to increase the binding avidity of many carbohydrate-based molecules and therapies from anti-microbials to anti-cancer agents. This increase in the number of carbohydrate molecules better mimics normal cellular structure and thus increases the effectiveness of the therapeutic and overcomes the low binding of single carbohydrate molecules. These traditional multivalent glycoconjugates are presented on scaffolds based on either an aromatic central core or cyclic peptide chains such as polylysine or RAFT's (Regioselective Addressable Functionalised Templates).[1,2] However, these peptide-based scaffolds can be subject to rapid degradation due to natural peptidases and fast clearance due to small size.[3]

We have developed a novel peptidomimetic which consists of a peptide squaramide hybrid termed 'squaratide' which possesses many potential benefits to traditional cyclic peptide scaffolds which includes better *in vivo* stability, potentially better interactions through hydrogen bond donation and accepting ability, straightforward and versatile synthesis unlocked through solid phase peptide synthesis. These squaratide scaffolds can then be conjugated with specific glycans to target the unusual glycosylation pattern on tumour cells and exploit the Warburg effect and thus unlock the potential for specific drug delivery to tumour cells. This poster will provide an overview of the early phase synthesis of these novel glycoconjugates.

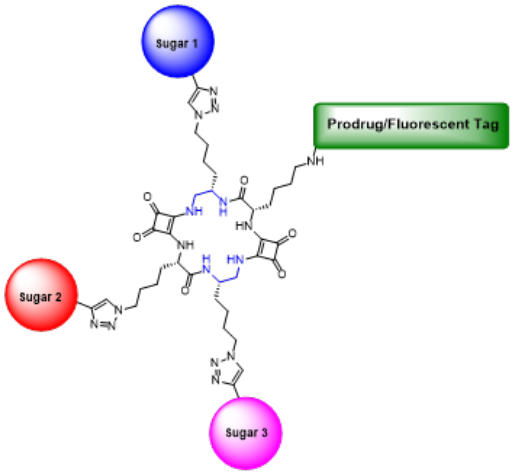

Figure 1. Generic proposed structure of the SBG's with potential fluorophore/prodrug attachment

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Can carbon dots be used as nanocarrier scaffolds?

Y. Z. Yingru Zhou [1], A. C. Adalberto Camisasca [1], M. B. Michał Bartkowski [1], A. W. Anita White [2], A. E. Alexander Eustace* [2],S. G. Silvia Giordani * [1]

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Confronting the toxicity, imprecise targeting, and increased drug resistance associated with current chemotherapy, which often results in severe side effects and suboptimal treatment outcomes, the development of carbon-based drug delivery systems (DDS) has emerged as a powerful solution. Among carbon nanomaterials, carbon dots (CDs) stand out as a focal point of investigation. Their small size, aqueous solubility, tunable photoluminescence, versatile surface functionalisation, and high biocompatibility underscore their potential as DDS.

We synthesised CDs from coffee grounds (CGs) using a chemical oxidation method. The resulting CG-CDs exhibit tunable fluorescence emission, with a maximum centered at 448 nm under excitation at 330 nm, and high stability over two hours of continuous illumination. Subsequently, we conducted pre-clinical *in vitro* assessments, revealing a concentration-dependent anti-proliferative effect in mammalian cancer cell lines. For concentrations up to 30 µg/ml, more than 80% cell viability was observed after a five-day incubation period. Furthermore, by applying drug resistance pump inhibitors, sulindac and elacridar, we confirmed that CG-CDs are not affected by the drug efflux pumps MDR-1 and P-gp. This finding further supports the potential of CG-CDs to effectively deliver chemotherapy drugs susceptible to drug efflux pumps.

Furthermore, we successfully demonstrated the uptake of CG-CDs by cancer cells through cellular localisation and internalisation studies. Confocal laser scanning microscopy revealed the accumulation of CG-CDs in the cytoplasm, with levels increasing over time. Our current aim to utilise CG-CDs as drug delivery scaffolds to enhance the efficacy of existing anti cancer drugs while reducing their side effects.

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Towards Phosphorus Cations as Main Group Catalysts

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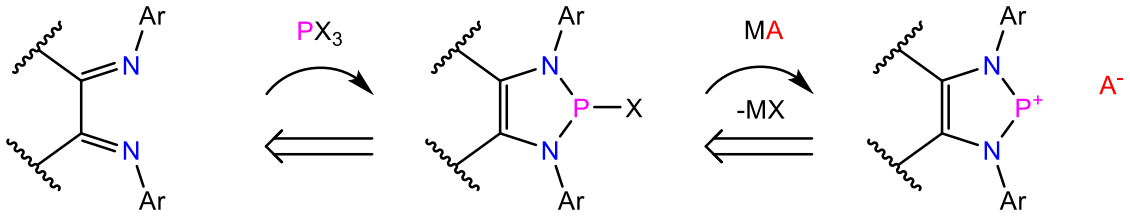
University College Dublin, Belfield, Dublin

Dependence on an ever-dwindling supply of transition metals (TMs) for their catalytic ability necessitates research into the development of candidates based on more-abundant elements.[1] Phosphenium cations (3), divalent phosphorus centres with a positive charge, have been shown to be effective main group catalysts in reactions such as imine reductions and hydroborations and are of interest for their potential in Frustrated Lewis Pair (FLP) chemistry.[2] The aim of this work is to determine the catalytic viability and potential scope of a number of phosphenium cations through the synthesis and subsequent analysis of catalytic candidates, with the view to provide viable alternatives to their well-established and widely employed TM counterparts.



Diimine Ligand (**1**) Phosphine Halide (**2**) Phosphenium Cation (**3**)

The phosphenium cations presented here are elements of a particular subset referred to as N-heterocyclic phosphenium cations (NHPs), characterised by the formation of a 5-member aromatic ring. Isolation of phosphenium cations involved synthesis of α-diimine ligand backbones (1), insertion of phosphorus centres through reaction with phosphorus trihalides and subsequent salt metathesis reactions to exchange the strongly coordinating halides with weakly coordinating anions (A^-).[3] A number of novel diimine ligands, phosphine halides (2) and phosphenium cations were synthesised. It is hoped that this work will add to the library of existing phosphenium cations, as well as provide the reactivity studies required for the determination of their catalytic viability.

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Development of a Portable and User-Friendly Enclosed System with Smartphone Camera Detection for Identifying Microplastics in Urban Water Runoff

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Urban stormwater runoff is a major source of microplastic pollution, significantly threatening ecosystems and human health[1]. Developing an efficient and quick on-site system to detect and measure microplastics in urban stormwater runoff is crucial to better understand the sources of microplastic pollution in urban areas. This method can provide quick preliminary results, which may eventually replace traditional microscopy analysis.

An enclosed 3D-printed case was designed as an innovative imaging system. It is equipped with a blue light-emitting source and an orange light correction filter that blocks blue light. This system uses fluorescent staining of microplastics and smartphone detection. The case was printed on a Raise Pro 3D printer using black PLA material. The samples were subjected to organic matter digestion, density separation to remove inorganic matter and size fractionation. Four solvents were evaluated for their effectiveness in staining microplastics and whether they caused their degradation. The microplastic particles were stained directly on the filter and in solution. Images were taken of the entire membrane filter area with a smartphone camera. The preliminary results revealed concerning levels of microplastic pollution in stormwater runoff in urban areas in Dublin. Most microplastic particles found were less than 100 µm in size. The system developed in this study offers a user-friendly, simple, and portable alternative to traditional microscopy for analysing microplastics in water runoff samples.

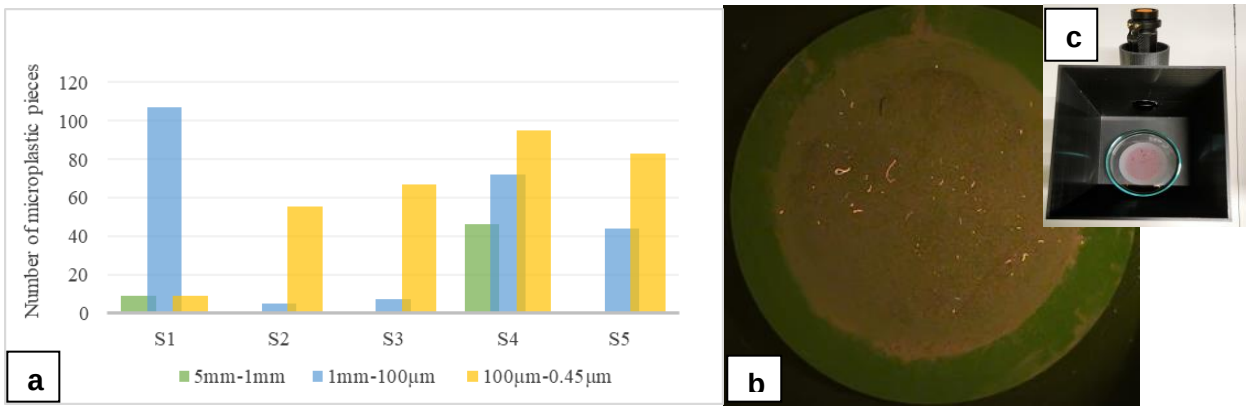

Figure 1 a) Characterizing Microplastic Distribution in Urban Water Runoff. Samples S2 and S3 were collected from building downpipes; S1 (construction site), S4 (next to sports ground), and S5 (Bus stop roadside drain) were collected from puddles; b) A cellulose nitrate membrane filter containing fluorescent particles (100 µm – 1mm); c) A 3D-printed case containing the filter (from image b) with microplastic particles.

References:

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Stereoselective 1,2-*cis*-glucosylations

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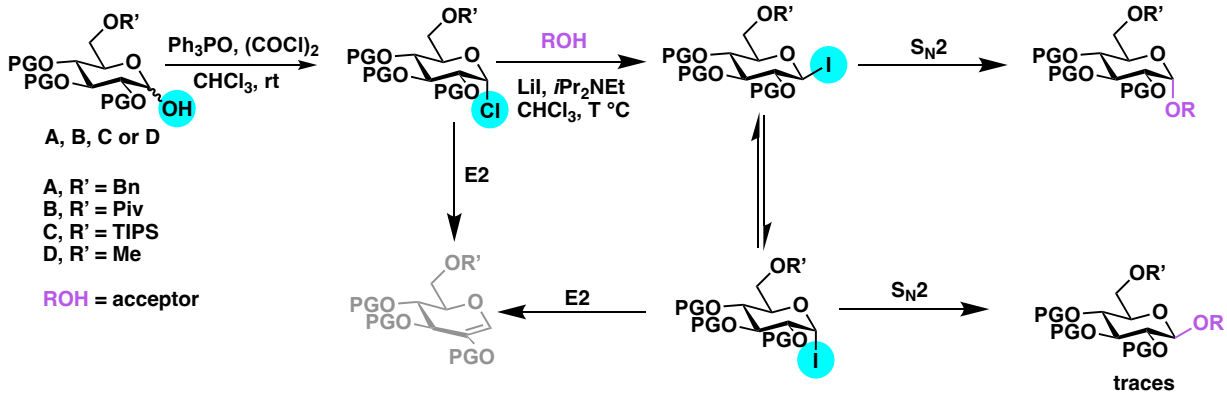
Oligosaccharide synthesis, consisting of multiple glycosylation steps, poses many difficulties with respect to regio- and stereoselectivity. [1] Depending on the reaction conditions, 1,2-*cis*- or 1,2-*trans*-glycosides can be obtained, of which the former are usually more difficult to synthesize. Previously, the McGarrigle group reported access to 1,2-*cis*-glycosides, by treatment of the glycosyl hemiacetal donor with Denton's catalytic Appel conditions, followed by reaction with LiI, *i*Pr$_2$NEt and the acceptor. [2,3,4] This procedure was successfully applied to the stereoselective synthesis of β-mannosides and β-rhamnosides.

In contrast to β-mannosides and β-rhamnosides, we will describe how glucosyl hemiacetal donors give α-glucosides. Glucosyl hemiacetal donors and a range of acceptors have been tested (**Scheme 1**). Optimization studies were required to prevent unwanted elimination of the glycosyl iodide intermediate to form the corresponding glucal side product (**Scheme 1**, grey). Changing the rate of addition of base *i*Pr$_2$NEt was found to limit the formation of the side product, affording an increase in the acceptor conversion, and still with an excellent *α/β* selectivity. To demonstrate the usefulness of the method, a target pentasaccharide was also synthesized using these conditions. [5]



Scheme 1. General scheme for the stereoselective synthesis of α-glucosides.

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VISIBLE-LIGHT-INDUCED CARBOSULFONYLATION OF ALKYNES

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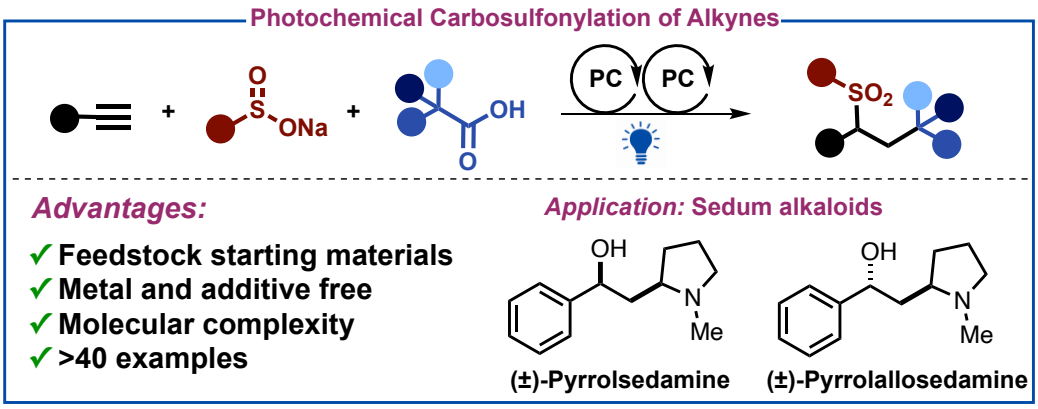
Organosulfur compounds are attractive scaffolds because of their numerous applications in medicinal chemistry, agrochemicals, material science and organic chemistry. Among them, sulfones are an important class of organosulfur molecules and versatile synthons in organic chemistry.[1] Furthermore, sulfur is found more frequently than fluorine in drug molecules and recently alkyl/vinyl sulfones have been found to act as radical precursors in synthetic organic chemistry. Due to their importance in various fields, many synthetic strategies have been developed to synthesise sulfone-containing molecules.[2] Among them, radical sulfonylation is one of the most efficient approaches to access functionalized sulfones with high step- and atom-economy.[3] Recently, visible light-promoted reactions have played a promising role in organic synthesis because of demonstrated complex bond constructions under mild reaction conditions and visible light is environmentally benign.[4] In this context, in the present project we focus on the radical difunctionalisation of alkynes under ambient conditions to access highly functionalised sulfones. In this poster, we will present our recently developed sustainable metal-free three-component carbosulfonylation of alkynes with arylsulfinates under photochemical conditions.[5] We have also applied our carbosulfonylation to the synthesis of sedum alkaloids.



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Synthesis of Gamma-Lactones from Epoxides and Ketenes

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γ-Lactones **1** are a component of 10% of all natural products (Figure 1) [1]. The γ-lactones have been synthesised in our lab through a new catalytic intermolecular reaction. An epoxide and a ketene are the two starting material substrates used by our group in the synthesis of γ-lactones. γ-Lactones have been reported to have multiple functions. The Corey lactone is an intermediate in prostaglandin synthesis [2]. Another example of the use of a γ-lactone is in the synthesis of Gemcitabine, which is a nucleoside analogue [3]. Costunolide is an anti-cancer, anti-fungal and anti-viral agent, with the γ-lactone moiety being key to its biological activity [4].

Baba et al synthesised a γ-lactone from diphenylketene and styrene oxide through Ph_4SbBr catalysis [5]. However, the catalyst used in this reaction is toxic and the scope of the reaction is quite limited. Hence, further research has gone into the synthesis of γ-lactones by using a less toxic catalyst, with the ultimate plan to develop a stereoselective variant of broad substrate scope. Our group has explored different catalytic systems. It was concluded from our preliminary studies that LiI is the optimal catalyst for the desired reaction.

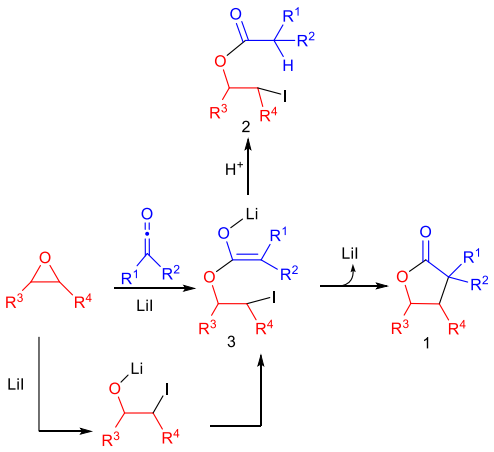

Figure 1: Proposed synthesis of γ-Lactones

A wide range of epoxides have been investigated for the reaction shown in Figure 1. The study of this reaction showed that under appropriate conditions the γ-lactone **1** was formed in good yield. However, with certain epoxides an acyclic ester product **2** was formed (derived from enolate intermediate (**3**)). The epoxide scope was studied by using diphenylketene or ethylphenylketene as the reactant partner.

Further research is being carried out to enable cyclisation of the ester enolate intermediate **3**, for those examples where cyclisation does not currently readily occur. We will present our preliminary results on the new synthetic methodology.

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Tungsten Carbide: A High-Efficiency Electrocatalyst for Hydrogen Evolution Reaction (HER)

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The development of efficient catalysts for the hydrogen evolution reaction (HER) is vital for advancing hydrogen production, a key component in the transition to sustainable energy [1]. Tungsten carbide (WC) is a promising electrocatalyst for HER, but its potential is often limited by slow kinetics due to the strong tungsten-hydrogen bond. This study explores the synthesis and electrocatalytic dynamics of WC in both acidic and basic media.

WC was synthesized using a solution chemistry route with tungstic acid, followed by annealing at in N_2 atmosphere. After confirming the successful synthesis of WC, subsequent electrocatalytic investigations were conducted. Detailed kinetic insights were obtained through linear sweep voltammetry (LSV) and cyclic voltammetry (CV) studies, providing information on superior current density (j), Tafel slope values, capacitance (C_{dl}) measurements, and electrochemical active surface area (ECSA).

The electrocatalytic performance of lab-synthesized WC and commercial WC was compared. Lab-synthesized WC exhibited superior performance, with lower onset potential, improved stability, lower Tafel slope, and higher electrochemical active surface area (ECSA) in both pH environments.

The findings highlight the efficiency and cost-effectiveness of the synthesis method and the potential of WC as a robust electrocatalyst for HER, suitable for diverse pH conditions. This research contributes significantly to the development of sustainable electrocatalysts for clean hydrogen production technologies.

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Computational studies, design and synthesis of Tau protein fragments, to explore a potential role in Alzheimer's disease

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Neurodegenerative diseases (NDDs) affect millions of people and there are currently insufficient drugs to prevent or treat these conditions. The most common NDD is Alzheimer's disease (AD) and the main symptom is dementia or memory deficit. The causes are still unknown but AD is correlated with alteration of brain cells and proteins such as Tau. The function of Tau protein is the assembly and stabilization of microtubules, which help normal neuron functions. In AD, this protein loses that capacity and does not bind microtubules, due to posttranslational modifications such as phosphorylation at a serine residue, which can result in misfolding. [1] Moreover, if the phosphoserine is close to a lysine, it might give a highly reactive dehydroalanine (Dha) residue, capable of crosslinking with glutathione or Lys, His and Cys residues.

Here, a ranking of 10 structures was obtained based on the Protein Databank (PDB) Tau 6HRE structure (Fig.1A). A Tau protein library has been prepared from the PDB and was analysed to identify proximate Ser and Lys residues (Fig. 1B). The stability analysis of these structures was studied in explicit solvent with NAMD, a molecular dynamics programme (Fig. 1C) Subsequently a peptide target was identified, the route was designed and prepared by solid-phase peptide synthesis (SPPS) methods (Fig.1D). The novel phosphoserine peptides may help to identify new potential therapeutic targets. The results of our studies to date will be presented.

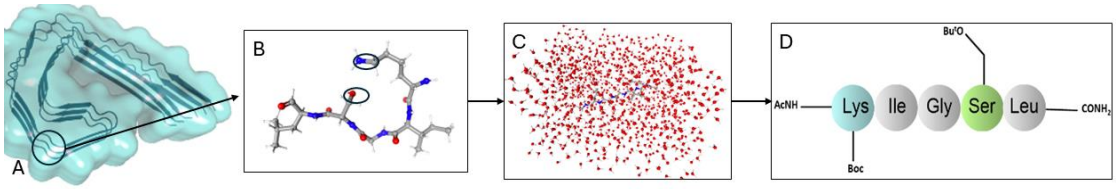

FIGURE 1. A) Tau protein; B) Distance selected; C) Tau fragment in a water box; and D) Peptide sequence synthesised

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Exploration of synthetic strategies for the development of non-planar atropisomeric porphyrins

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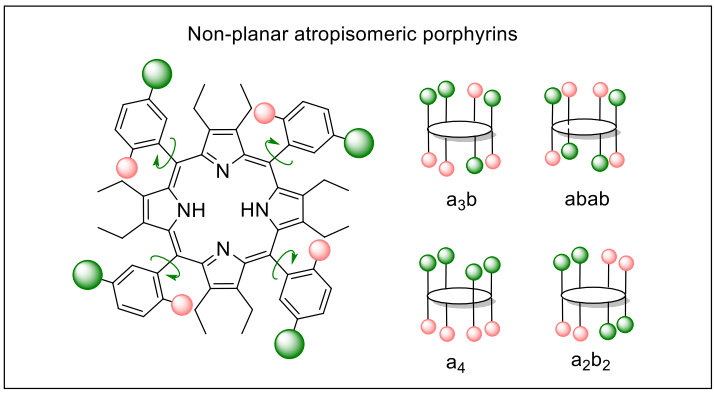
Atropisomers are a subclass of conformers arising from restricted rotation about a C–C single bond, predominantly due to steric hindrance. This phenomena has been exploited in porphyrins for applications ranging from sensing [1] to biomimetic models. [2] Work has also demonstrated the significance of tetrapyrrole atropisomerism in medicine, reporting the enhanced phototoxicity of the α_4-atropisomer in comparison to the other three atropisomers of Redaporfin©, a pre-clinical bacteriochlorin photosensitizer. [3] Overall, atropisomeric porphyrins offer routes to easily adaptable, yet complex systems due to the wide variety of possible peripheral functionalities, compounded by the multiple environments that each atropisomer can provide, which allows for precise control of the internal and external environments.

Whilst the above examples provide a glimpse into the potential impact of utilizing atropisomerism, [4] studies are still required to fully understand the fundamental mechanisms in tetrapyrrole systems. This work therefore describes the synthesis of a library of non-planar atropisomeric porphyrins with various peripheral functionalities, which has allowed us to comprehend the relationship between structure and atropisomer stability.



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C-C bond formation in a sterically demanding environment

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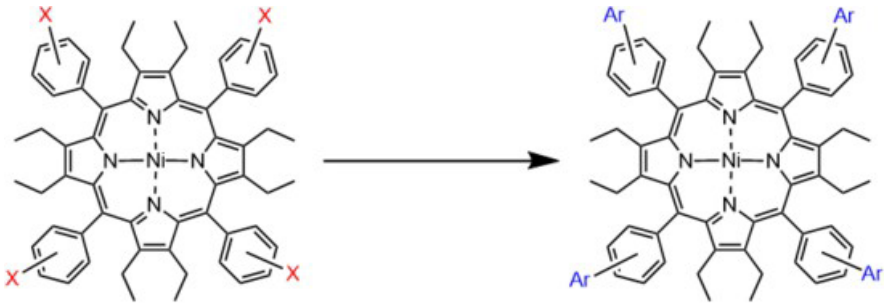
Nonplanar porphyrins are porphyrins which undergo macrocyclic distortion due to steric repulsion in the core of the macrocycle or overloading the periphery of the porphyrin with sterically demanding groups. Dodecasubstituted porphyrins where the periphery of the porphyrin is fully substituted often exhibit saddled conformations. This class of nonplanar porphyrins has been found to be useful in molecular recognition, organo- and photoredox-catalysis. [1] This is a result of the nonplanar framework allowing guest molecules to interact directly with the core. [2] These functions can be enhanced by decorating the porphyrin with functional groups with varying electronic and steric modifications to achieve these functional materials. [3] Unlike their planar counterparts, classic synthetic protocols for C-C bond forming reactions of non-planar porphyrins are underdeveloped. Here we present synthetic advances towards nonplanar dodecasubstituted porphyrin with robust architectures designed as enzyme mimic precursors. The synthetic details of C-C couplings performed in the sterically demanding environment of *ortho*-, *meta*-, and *para*- positions of dodecasubstituted porphyrins will be presented. The methodological advances will open a new door for the functionalization of nonplanar porphyrins and facilitate accessing new molecular shapes and functions.



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BODIPY-anthracene dyads as versatile photosensitizers

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Boron dipyrromethene (BODIPY) dyes as highly fluorescent molecules were first synthesized in 1968[1] and have drawn considerable attention as fluorophores. Their photosensitizing capability has led to extensive research aiming to develop new derivatives for diverse applications, including photodynamic therapy (PDT). Therein, the interaction between light, biological matter and a photosensitizing species is utilized to induce cell death which provides an effective therapeutic method to treat diseases such as cancer.

The principle of PDT relies on the formation of triplet excited states, from where reactive oxygen species (ROS) acting as local cytotoxins are generated. Until recently, BODIPY triplet sensitizers depended on the presence of heavy atoms. The introduction of a donor unit, like anthracene, to the BODIPY periphery (Fig. 1) enables the generation of triplet states *via* photoinduced electron transfer (PeT). Moreover, the resulting $^1O_2$ can react with the anthracene moiety to form highly fluorogenic photoproducts.[2] Therefore, these BODIPY dyads can act as both emitters and sensitizers. Lastly, the decay pathway after exciting the molecule into the singlet excited state, i.e., radiative emission *vs*. nonradiative intersystem crossing, can be tuned by the choice of either non-polar or polar solvent medium, respectively.[3]

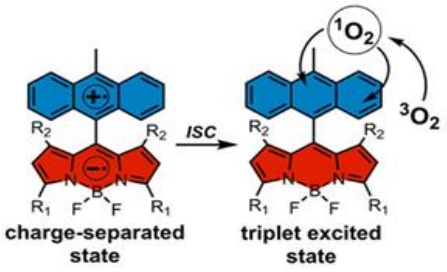

Fig. 1: A representative of the BODIPY-anthracene dyad.

Here we present the synthesis and characterization of BODIPY-anthracene dyads (BADs) with unsymmetrical substitution patterns as functional dyes with switchable intersystem crossing and potential applications in PDT. [4]

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TOWARDS AUTOMATED SYNTHESIS OF MONOSACCHARIDE BUILDING BLOCKS AND APPLICATIONS IN OLIGOSACCHARIDE SYNTHESIS

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Developing effective techniques for synthesising carbohydrates with complex structural organisation is crucial to the discipline of glycoscience. Despite significant progress in the synthesis of oligosaccharides, the synthesis of targets featuring complex glycosidic linkages of monosaccharide building blocks remains a challenge.While much of the emphasis in the development of automated platforms for carbohydrate synthesis has been on the construction of oligosaccharides, manual syntheses of monosaccharide building blocks can represent up to 90% of the synthetic effort and thus constrain throughput[1]. This is often laborious and time-consuming. Furthermore, excess amounts of glycosyl donor building blocks are frequently used in glycosylations, presenting a pressing need to develop methods for streamlining the acquisition of monosaccharides.

The aim of this work is to improve the purification of monosaccharides, which is often a bottleneck in the preparation of important carbohydrates. By using a purification tag, TIDA,[2] the process of purifying monosaccharides can be made simpler and more efficient. One of the key findings of this research is that the silica binary affinity properties of the TIDA tag can be extended to monosaccharides bearing a variety of protecting groups. This characteristic proved beneficial during the synthesis of the tagged molecules, as it simplified purification and eliminated the need for arduous column chromatography. As a result, this process is potentially amenable to automation. Additionally, the tagged building blocks have been used to synthesise a trisaccharide in high yield, indicating that the TIDA tag is appropriate for the synthesis of oligosaccharides.

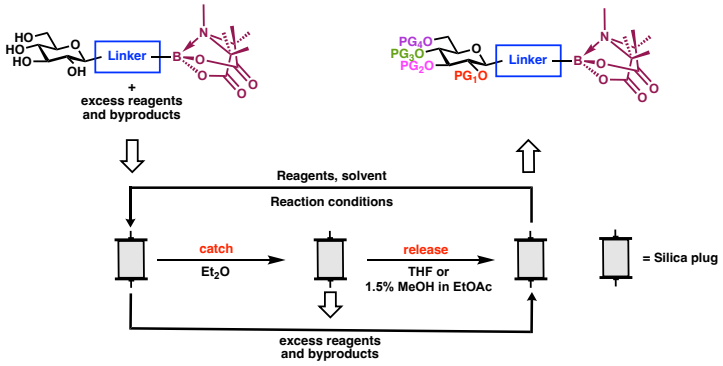

Figure 1: Catch and release purification

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New insight into organic solid solutions using low-frequency phonon analysis

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Solid solutions are solid phases with the characteristics of a solution.[1] By precisely adjusting their stoichiometry a wide range of properties can be finely tuned, including thermal and chemical stability, piezoelectricity, photochromism, hardness, and more. [2, 3]
To a large extent, these disordered phases show increased lattice energy, which is stabilized by the increase in entropy upon mixing.[1] If the former can be directly measured by thermal analysis, the latter is more subtle. In particular, vibrational entropy, which is related to the "stiffness" of bonds and interactions, may be investigated by phonon dispersion curves. [4, 5]
This work focuses on the synthesis and polymorph control for solid solutions of substituted aspirin, and their phonon analysis by Raman spectroscopy. Two polymorphic solid solutions (SS-I and SS-II) of chloro and bromo substituted aspirin (ClA)x(BrA)1-x were prepared in the compositional range of x = 0 to1 using slow solvent crystallization and by reaction crystallization respectively. X-ray diffraction analysis (SC-XRD and PXRD) and thermal analyses (TGA and DSC) were used to characterise the chemical and structural identity uniformity of the products.
Variable temperature Raman spectroscopy was performed on single crystals of the solid solutions to obtain low-frequency phonon spectra between temperatures (-14 °C) to (80 °C) as a function of composition and temperature. Remarkably, composition and temperature variation act on different phonon modes, though in both cases a continuous shift was observed. Further experimental and computational studies are ongoing to correlate and quantify vibrational entropy in solid solutions.

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pH-Responsive Hydrogel Micro-Actuators

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In the last decade, advancements in additive manufacturing have enabled the fabrication of robotic tools on the microscale, that find application in microfluidic devices, wearable flexible electronics and micro-robotics[1]. In this work, we present polymer micro-actuators powered by pH-responsive hydrogel structures fabricated *via* two-photon polymerisation (2PP). Using 2PP, it is possible to control the chemical and mechanical properties of these micro-actuators depending on the fabrication parameters[2].

Herein, we propose a microgripper design, where the actuation of the gripper is controlled by the swelling of pH-responsive blocks incorporated into the design. Their shape transformations were due to the hydrogel's ability to contract and expand in response to pH change of the environment. To cover a relatively broad pH range, two pH-responsive hydrogel formulations were selected, based on weak acid and weak base monomers, respectively. The successful fabrication and alignment of multi-material microstructures was assessed by scanning electron microscopy (SEM). The swelling properties of the hydrogel blocks was characterised by optical microscopy and atomic force microscopy (AFM). The performance of the micro-actuators was investigated in terms of design, photoresist formulation and applied fabrication parameters, and this can be further tuned for the intended applications.
Such micro-tools can be applied in sensor devices, microfluidics for flow manipulation and control, and for the realisation of novel micro-surgical tools[3, 4].

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Bio-Inspired Photonic Actuators

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Nature achieves its colour-changing abilities predominantly through the phenomenon of structural colour. Through this, colour is reflected by high refractive index materials containing microstructures with sizes and periodicity comparable to wavelengths of light. The distance between these microstructures can be altered allowing animals like the chameleon to change their colour at will. [1]

These structurally coloured materials found in nature have been replicated synthetically through extrinsic or intrinsic ordering. Extrinsically ordered materials are produced using additive and subtractive manufacturing techniques such as etching, e-beam lithography, and nanoimprint lithography. Intrinsically structured materials have been achieved through self-assembling materials such as liquid crystals, colloidal particles, and sol-gels. To achieve multilevel order and disorder, both these approaches can be combined through the use of self-assembling nanomaterials and Direct Laser Writing (DLW). This enables the creation of complex optical devices.[2][3]

The self-assembling material used in this work is a functionalised cellulose, Hydroxypropyl Cellulose. This material produces structural colour due to the helical ordering; the reflected colour is dependent on the spacing between the ordered layers.[4] The cellulose is functionalised further to create crosslinking sites between the chains, allowing structures to be printed in the material using DLW. The resulting structures exhibit a wide gamut of structural colour in response to hydration, temperature, and ion concentration. Hydration increases the repulsion between the cellulose chains creating a red shift in the reflected colour. Temperature affects the colour due to the lower critical solution temperature (LCST) of the biopolymer.. This work presents DLW with nanocomposite cellulose materials as a route to produce high-precision microstructures with tuneable colour.

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Lunar Regolith and Anti-Adhesion Nanostructures

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Lunar regolith currently poses one of the greatest challenges to lunar exploration. Following Appollo 17, astronaut Gene Cernan observed that lunar dust was a far more significant issue than originally anticipated, stating “dust is probably one of our greatest inhibitors”[1]. This is due to the extensive issues that lunar dust caused on the Apollo missions for both the equipment and the health of the astronauts. Equipment related issues included seal failures, clogging of mechanisms and false readings[2]. As well as this, the lunar dust caused great vision obstruction and astronaut Harrison Schmitt commentated that he experienced “lunar hayfever” as a reaction to the dust. In addition, significant cell toxicity in both lung and neuronal cell lines have been linked to exposure to this dust[3].

Lunar regolith is composed of unconsolidated rock material and covers the entire surface of the moon, several meters in depth. This loose, abrasive and jagged material is a result of sustained asteroid bombardment over millions of years[4]. Lunar dust is roughly 20% of regoliths weight and is categorised as any particle less than 20 µm. Due to the extensive range of issues associated with lunar dust great efforts have been made to reduce the adhesion of these particles to surfaces. These methods include both active and passive systems. Active systems include brushing and electrodynamic dust shielding, and are generally less sustainable than passive systems[5]. A prime example of passive anti-adhesion that can be found in nature is the “Lotus effect”. This effect describes the Lotus plant’s ability to “self-clean” due to the topography of the surface of its leaves. Inspired by nature, efforts have been made to reduce the materials surface energy for particle adhesion mitigation.

The work of the Kelleher group focuses on developing nano and microstructured surfaces for antibacterial and antibiofouling surfaces inspired by nature. The aim of this project is to demonstrate further applications of these anti adhesive surfaces as observed in nature. With the use of two photon polymerisation and replica moulding techniques, a variety of patterns were easily fabricated. These structures have the potential to reduce surface contact area with the regolith particles and therefore reduce Van der Waals forces[6]. As well as this the structures can increase the hydrophobicity of surfaces and therefore reduce the surface energy. An investigation into the potential anti fouling effect of these Nanoscribe printed structures is underway.

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Mechanobactericidal Polymer Surfaces for Medical Devices – Synthesis and functionalisation of poly(2-allyloxymethyl-2-ethyltrimethylene carbonate) (PAOMEC)

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Creating surfaces with micro- or nano-scale structures on them has been shown to kill or repel bacteria using topography alone.[1] This may provide an alternative method to broad-spectrum antibiotics for prevention of bacterial infections upon medical device implantation. This is particularly important with the increasing threat of antimicrobial resistance.[2]

Poly(2-allyloxymethyl-2-ethyl-trimethylene carbonate) (pAOMEC) is a polycarbonate with a biodegradable backbone that can be functionalised post-polymerisation.[3] These characteristics make pAOMEC the ideal polymer to investigate how varying the surface properties using short chains with an array of functional groups can affect the antibacterial nature of the material.

A UV-initiated, free radical polymerisation is used to fabricate the nanostructured mechanobactericidal surfaces. Bacterial cell testing is then completed to investigate these nanostructured hydrophilic, hydrophobic, cationic and anionic materials.

This poster presents the early stages of this research including the synthesis and crosslinking of PAOMEC and preliminary analysis of functionalised crosslinked materials.

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Composite polymer microstructures fabricated via direct laser writing for structural colouration and analyte sensing

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Over the past few decades, synthetic structural colouration using composite materials has garnered great interest in many different fields. Structural colouration has been achieved both on the micro- and macro-scale by combining a series of different materials, including silica nanoparticles[1], cellulose nanocrystals[2], and liquid crystals[3], to name a few.

Herein, we propose a novel approach for achieving structural coloration at the microscale, by employing nanocomposite photoresists for microfabrication by direct laser writing (DLW). The nanocomposite photoresists were based on polymer nanoparticles incorporated into compatible monomeric photoresists at sufficiently high concentrations to promote self-assembly. By combining such photoresists with DLW, microstructures with a full gamut of tuneable structural colours can be fabricated, without having to change either nanoparticle dimension or the materials for refractive index change. This tunability is brought by DLW, and more precisely, by the ability to finely tune the fabrication parameters, such as laser power, slicing and hatching distance, which in turn affect interparticle distance, and hence the reflected colour. Additionally, by employing stimuli-responsive materials as the host for the polymer nanoparticles, the structural colour can be further modulated post-fabrication by introducing the stimulus of interest.

To conclude, the work shown herein demonstrates a novel time- and cost-effective method for the fabrication of responsive photonic microstructures with easily programmable colour change and functionality. Such structures could find applications in sensing technologies, biomedical engineering[4] and environmental monitoring[5].

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Instability of RNA Mitigated by Reversible Ribose 2'-OH Acylation

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The instability of RNA presents serious challenges for the development, analysis, storage and transportation of emerging vaccines and therapeutics.[1] Degradation of RNA can occur through spontaneous thermal fragmentation, or can be catalysed by ubiquitous ribonuclease enzymes. In both cases, nucleophilic attack of the ribose 2'-hydroxy group on the adjacent phosphodiester linkage is the predominant mechanism of degradation.[2] Hence, designing a chemical modification strategy to selectively mask the 2'-OH functional group in a reversible manner will allow for enhanced thermal and enzymatic stability, extending the functional half-lives of RNA-based pharmaceutical products.[3]

Here, we present reversible 2'-OH acylation as a pro-drug type strategy for the stabilisation of RNA. A series of acylating agents have been synthesised and reacted with RNA strands *in vitro*. Characterisation by MALDI-TOF MS and HPLC confirmed formation of the desired modified RNA products. Removal of acyl groups and recovery of native RNA occurs under mild conditions found within cells. Ongoing work examines the storage stability of acylated RNA formulations, kinetics of acyl group removal, and the effect on protein production using longer mRNA models. This novel method promises to further advance the development of RNA-based therapeutics for patient treatment.

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Fabrication of Electrospun Membranes for Water Filtration

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Membranes are essential in industry to produce clean water for use in industrial processes. However, many membranes become fouled with bacteria which is often irreversible. This can lead to the requirement for new filters as they cannot be reused due to biofilm formation on the surface of the membrane. [1] This project aims to produce electrospun fibre mats that can function as membranes which are both antibiofouling and antibacterial by embossing micro and nanostructures on the membrane surface. This could prevent biofilm formation on the surface of the membrane due to the antibiofouling properties shown by micropatterned surfaces, and the antibacterial properties of nanopatterned surfaces. [2,3] Adding these properties to the membrane should allow the membrane to work for a longer period before replacement would be necessary.

This work will show how these membranes are fabricated and the optimisation involved in creating the membranes. Polysulfone is electrospun to create a fibre mat and 8 of these mats are then compressed under controlled conditions to create a membrane. Tests are then carried out to ensure that the membranes function effectively, these include using a stirred cell to determine the flux and fluorescently labelled polystyrene beads of 10 µm, 0.5 µm and 0.1 µm to determine the percentage rejection which can be linked to the pore size of the membranes. [4] The membranes have also been successfully structured with both a micro and nano pattern respectively which has been shown with SEM images.

The work will also introduce future work which will involve bacterial cell testing of both the planar membranes and structured membranes to determine if they are antibacterial and antibiofouling for Gram-positive and Gram-negative bacterial strains.

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Degradation of Perfluorooctanoic Acid by Plasma-Assisted Catalysis in a DBD Reactor

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Per- and Poly-fluoroalkyl Substances (PFAS) are a sub-class of persistent organic pollutants, with broad applications including non-stick coatings, water-proof clothes, proton exchange membranes and fire-fighting foams. These substances resist natural degradation, accumulating in organisms and posing significant health risks to humans and animals, affecting the endocrine system, liver, kidneys, and reproductive health.[1, 2] Current removal methods involve adsorption, stabilization, and membrane-based techniques, all of which generate secondary waste streams which need to be treated separately. In situ degradation methods, including thermal, sono-chemical, advanced reduction, bioprocessing, and advanced oxidation processes, have been explored.[3] Of these, Non-Thermal-Plasma-Assisted Catalysis shows promise for PFAS breakdown, through reaction with reactive species generated within plasma. This offers potentially effective energy-efficient breakdown method without relying on oxidizing or reducing agents. This research focuses on the breakdown of Perfluorooctanoic Acid (PFOA) which is often used as a model PFAS for breakdown studies.

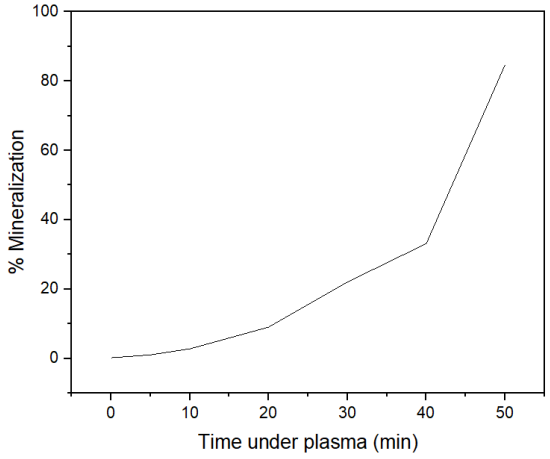

Fig. 1 % Mineralization of PFOA Vs time under plasma

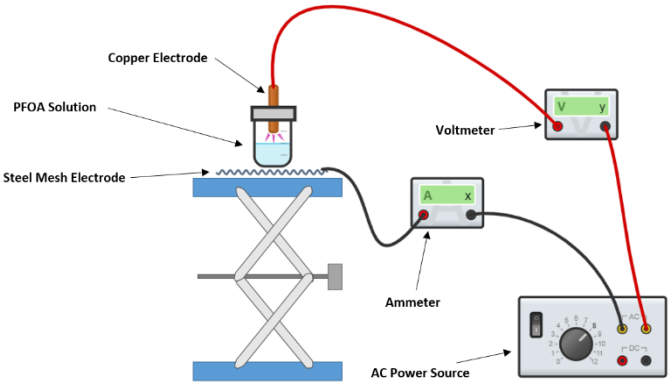

Fig. 2 Plasma reactor setup for PFOA degradation

The plasma reactor used was a Dielectric Barrier Discharge (DBD) plasma over 5 mL of 100 ppm PFOA. Various catalysts were screened. PFOA degradation was measured by LC-MS, and mineralization (total breakdown of PFOA to inorganic products) was measured using ion selective [F^-] analysis. Mechanistic studies were carried *via* addition of known radical sources and scavengers and observing the effect on reaction rate. The technique was applied to the real world problem of breaking down stockpiles of PFAS containing aqueous firefighting foams, and shows promise based off preliminary mineralization results

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