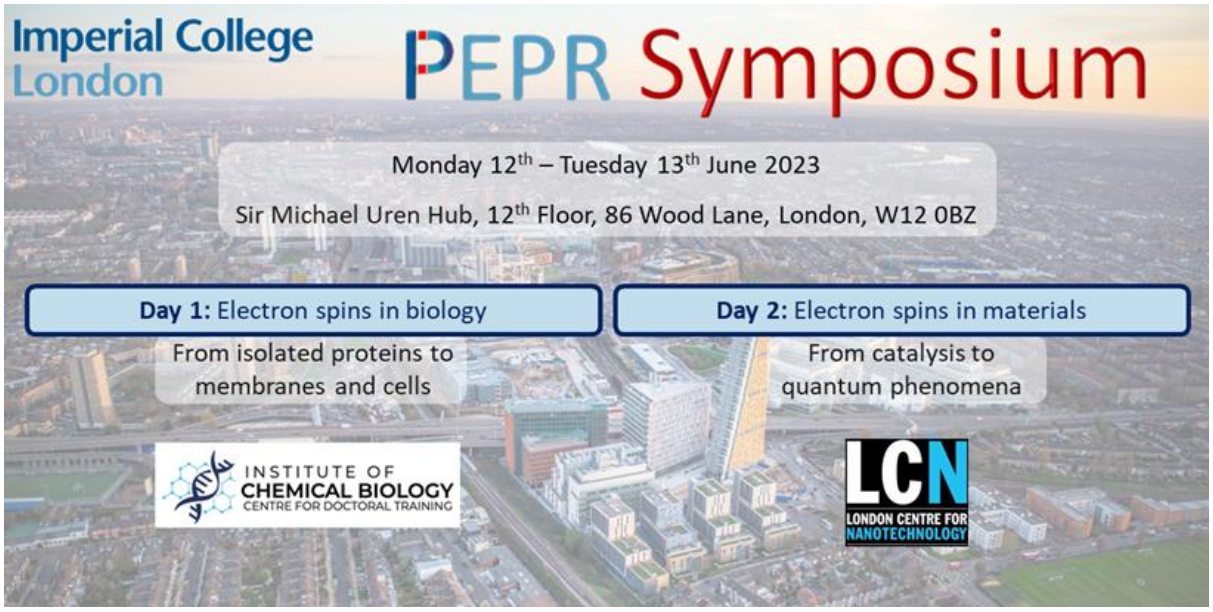

BOOK OF ABSTRACTS

PEPR Symposium 2023

12th – 13th June, Imperial College London, White City Campus

Programme

Imperial College London

PEPR Symposium

The power of electron spins in Biology and Materials

DAY 1: ELECTRON SPINS IN BIOLOGY *FROM ISOLATED PROTEINS TO MEMBRANES AND CELLS*

9:00 **Registration**
9:20 **Welcome**

Session 1: EPR in the era of cryo-EM

9:30 **Plenary: 30' + 5' Q&A**
Enrica Bordignon (*chair: Maxie Roessler*)
10:05 **Short Talks: 12' + 3' Q&A**
1. Alexey Potapov; **2.** M Teresa Bertran; **3.** Konstantinos Beis; **4.** Rivka Isaacson
11:05 **Discussion Panel**
Enrica Bordignon, Doryen Bubeck, Alberto Collauto, Kostantinos Beis (*moderator: Rivka Isaacson*)
11:25 **Coffee Break**

Session 2: Using EPR to investigate biological membranes

11:55 **Short Talks: 12' + 3' Q&A**
1. John Britton; **2.** Ben Almquist; **3.** Rupali Dabas (*chair: Jana Eisermann*)
12:40 **Discussion Panel**
Jana Eisermann, Oscar Ces, Nazila Kamaly, Rob Law (*moderator: Marina Kuimova*)
13:00 **Lunch Break**

Session 3: Exploiting intrinsic paramagnets

14:30 **Plenary: 30' + 5' Q&A**
George Cutsail III (*chair: Blaise Geoghegan*)
15:05 **Short Talks: 12' + 3' Q&A**
1. Eleanor Clifford; **2.** Kourosh Ebrahimi; **3.** Daniel Wilson; **4.** Silene Engbers
16:05 **Discussion Panel**
George Cutsail III, Guy Hanke, Kourosh Ebrahimi (*moderator: Maxie Roessler*)
16:25 **Poster Session & Drinks Reception**
18:10 **Talks and Posters Prizes, Closing Remarks**

DAY 2: ELECTRONS SPINS IN MATERIALS *FROM CATALYSIS AND ENERGY APPLICATIONS TO QUANTUM PHENOMENA*

9:00 **Registration**
9:15 **Welcome**

Session 1: EPR in catalysis

9:20 **Plenary: 30' + 5' Q&A**
Mario Chiesa (*chair: Maxie Roessler*)
9:55 **Short Talks: 12' + 3' Q&A**
1. Leah Webster; **2.** Marina Perez Jimenez; **3.** Molly Parry
10:40 **Discussion Panel**
Mario Chiesa, Mark Crimmin, Nick Long, Mark Chadwick (*moderator: Maxie Roessler*)
11:00 **Coffee Break**

Session 2: EPR in energy research

11:30 **Short Talks: 12' + 3' Q&A**
1. Bowen Ding; **2.** Yunfei Dang; **3.** Julianna Panidi; **4.** Teresa Insinna (*chair: Eric McInnes*)
12:30 **Discussion Panel**
Eric McInnes, Chun Ann Huang, Stephen Skinner (*moderator: Anthony Kucernak*)
12:50 **Lunch Break | PEPR AGM: 13:10 - 14:40**

Session 3: EPR to investigate light-induced phenomena

14:50 **Plenary: 30' + 5' Q&A**
Sabine Richert (*chair: Alberto Collauto*)
15:25 **Short Talks: 12' + 3' Q&A**
1. Jeannine Grüne; **2.** Sebastian Gorgon; **3.** Hanbo Yang
16:10 **Discussion Panel**
Sabine Richert, Neil Alford, John Morton (*moderator: Sandrine Heutz*)
16:30 **Poster Session & Drinks Reception**
18:15 **Talks and Posters Prizes, Closing Remarks**

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General information

	The **venue** is the Uren Building at the Imperial White City Campus. Closest tube stations are White City and Wood Lane.
	Please **arrive by 9 am latest** for registration. Should you arrive late, ask the receptionist. **Posters set up** will be during the coffee break. Please remember to take your poster down at the end of the day. If you **need to leave early**, note that the reception of the Uren hub is closed after 5 pm and a swipe card is needed to go through the turnstiles. We will arrange “human shuttle services” at 5:30 pm, 6 pm and 6:30 pm.
	Free **WiFi** is available throughout the College estate via Sky WiFi – connect to *The Cloud* from the available network list, open a browser and follow the instructions to register. Guests and visitors working for another participating organisation can also access the eduroam network.
	The Imperial Campus is **smoke-free**. Smoking is not permitted within 20 metres of Campus perimeters.

Electron Spins in Biology
From Isolated Proteins to Membranes and Cells

Oral contributions

EPR in the era of cryo-EM	**E. Bordignon**	**Biological applications of EPR in the era of cryo-EM**
	A. Potapov	Structure of human Ccr4-Not nuclease module based on AlphaFold-computed model and experimental data from X-ray crystallography and EPR distance measurements
	M.T. Bertran	Discovery of specific inhibitors and activators of PADI4 to elucidate its biological role
	K. Beis	Molecular mechanism and dynamics of SLiPT transporters
	R. L. Isaacson	Molecular Machinery for Proteostasis
Using EPR to investigate biological membranes	J. Britton	The effect of ethanol upon the function of respiratory complex I
	B. Almquist	Inorganic Transmembrane 'Proteins'
	R. Dabas	Redox-responsive, crosslinked polymeric nanogels for mRNA delivery
Exploiting intrinsic paramagnets	**G.E. Cutsail III**	**Elucidating Copper Active Sites in Biology with Advanced EPR Spectroscopies**
	E. Clifford	Probing a key semiquinone intermediate in the mechanism of respiratory complex I with EPR spectroscopy
	K. H. Ebrahimi	From Exploiting Paramagnetic [4Fe-4S] cluster to VITAS, a journey to antiviral natural product discovery
	D. W. N. Wilson	Electronic structure and bonding in heterometallic clusters inspired by the C-cluster of carbon monoxide dehydrogenase
	S. Engbers	Characterization of a Porphyrin Iron(III) π-Dication

Poster presentations

P1	J. Sawyer	Direct comparison of Light Induced Triplet-Triplet Electron Resonance (LITTER) spectroscopy with Förster Resonance Energy Transfer (FRET)
P2	J. Eisermann	The importance of membrane constitution – Impact of cardiolipin and ethanol on membrane fluidity
P3	J. Eisermann	The interplay of ROS production and lipid peroxidation on respiratory complex I function
P4	T. Wells	Purification and Characterisation of Hydrophobically Distinct Populations of Rubisco
P5	S. Engbers	Characterization of a Porphyrin Iron(III) π-Dication
P6	D. Facchetti	Ex-situ Protein Film Electrochemistry-Electron Paramagnetic Resonance (PFE-EPR): applications on the enzymatic complex "Methionine sulfoxide reductase QP" (MsrQP)
P7	M. Krishnamoorthy	Polyaniline - bismuth ferrite Based Nanocomposite Immobilized on Liquid Natural Rubber as Integrated Adsorbents-Photocatalyst for Removal of Ciprofloxacin Antibiotic

Biological applications of EPR in the era of cryo-EM

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Macromolecular protein assemblies are of fundamental importance for many processes inside the cell, as they perform complex functions and constitute central hubs where reactions occur. Generally, these assemblies undergo large conformational changes and cycle through different states that ultimately are connected to specific functions further regulated by additional small ligands or proteins. Unveiling the 3D structural details of these assemblies at atomic resolution, identifying the flexible parts of the complexes, and monitoring with temporal resolution the dynamic interplay between different protein regions under physiological conditions is key to fully understanding their properties and to fostering biomedical applications.

In the last decade, we have seen remarkable advances in cryo-electron microscopy (EM) techniques, which deeply transformed our vision of structural biology. Concomitantly, electron paramagnetic resonance spectroscopy (EPR) has benefited from methodological innovations which also improved the quality of the information that can be achieved. Such enhanced sensitivity widened their applicability to macromolecular complexes in environments close to physiological conditions and opened a path towards in-cell applications.

In this lecture I will focus on the advantages and challenges of EPR techniques within an integrative biophysical approach[1] towards a complete understanding of macromolecular structures and functions.

References

[1]Laura Galazzo and Enrica Bordignon (2023) Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 134–135, 1-19.

Structure of human Ccr4-Not nuclease module based on AlphaFold-computed model and experimental data from X-ray crystallography and EPR distance measurements

A. Potapov[1], M. Bartlam[2] and S. Winkler[3]

[1]School of Physics and Astronomy, Sir Peter Mansfield Imaging Centre, University of Nottingham, University Park, NG7 2RD, UK; [2] School of Pharmacy, Sir Peter Mansfield Imaging Centre, University of Nottingham, University Park, NG7 2RD, UK; [3]Nankai International Advanced Research Institute (Shenzhen Futian); College of Life Sciences; State Key Laboratory of Medicinal Chemical Biology, Nankai University, Tianjin, 300071, China.

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Recently, it became possible to predict protein structures based on their amino acid sequence using AI-based software (AlphaFold2 and RoseTTAFold). This advancement may potentially revolutionise the field of structural biology because the procedure for obtaining a structural model becomes less demanding.

Previously, structural models were constructed using computational tools which used experimental data as an input. However, when the input data is incomplete, such an approach becomes problematic. Instead, with the structure prediction software, a structural model can be obtained without any experimental data at all. The role of the experiment then is to validate this purely computational model.

In this work we present how such an approach helps in improving a model of a human Ccr4-Not nuclease module based on the data from X-ray crystallography and EPR distance measurements. The Ccr4-Not complex is involved in the regulated degradation of mature cytoplasmic mRNA, which is a key step in eukaryotic gene regulation. While some parts of Ccr4-Not structure have been resolved by X-ray crystallography, its complete structure has not been solved. In particular, the position of the EEP domain in the complex is unknown. To find its position, we overlay the incomplete experimental X-ray structure with the structure computed by the AlphaFold software. The predicted distance of 63.9 Å between the two nuclease sites in the complex is validated by the RIDME experiment which yields a distance of 64.9 Å. This indicates that the structure obtained by overlaying, provides an improved model of the human Ccr4-Not nuclease module.

Discovery of specific inhibitors and activators of PADI4 to elucidate its biological role

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Peptidyl Arginine Deiminase 4 (PADI4) is a member of the peptidyl deiminase family of proteins that catalyse the post-translational modification of arginine to the non-canonical amino acid citrulline. PADI4 is involved in various biological processes and its dysregulation has been linked to various pathologies, including rheumatoid arthritis and a range of cancers; however, the molecular mechanisms that regulate PADI4 are poorly understood [1,2]. In consequence, the discovery of chemical tools that selectively modulate PADI4 activity is crucial to understand its biological function.

The Random non-standard Peptide Integrated Discovery (RaPID) platform is a very powerful technology that enables us to screen > 1 trillion cyclic peptides against a target of interest [3,4]. We carried out three RaPID screens and identified macrocyclic peptides that bound to different conformations of PADI4 with nanomolar affinities. One of the peptides identified acts as a potent and selective PADI4 inhibitor both *in vitro* and in cells, while another one with no inhibitory effect was used as an affinity probe. In addition, we also identified a cyclic peptide that acts as a potent PADI4 activator at low calcium concentration. These peptides will be used as chemical tools to modulate PADI4 activity and hence elucidate its biological role.

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Molecular mechanism and dynamics of SLiPT transporters

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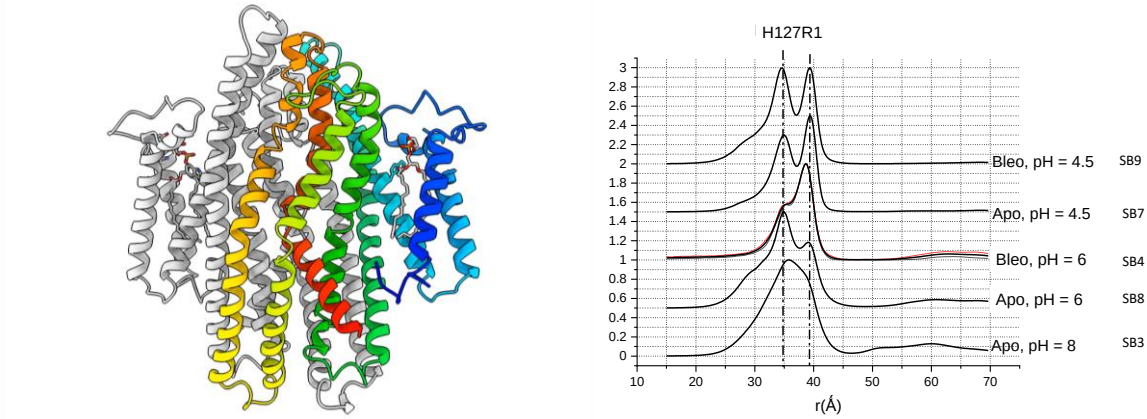
Antibiotic metabolites and antimicrobial peptides mediate competition between bacterial species. Many of them hijack inner and outer membrane proteins to enter cells. Sensitivity of enteric bacteria to multiple peptide antibiotics is controlled by the single inner membrane protein SbmA. To establish the molecular mechanism of peptide transport by SbmA, we determined its cryo-EM structure in two different conformations. The structures show a novel fold, defining a new class of secondary transporters named SbmA-like peptide transporters (SLiPT). SLiPT transporters are proton driven as established in proteliposome transport assays. PELDOR measurements show how protons are coupled to conformational changes along the transport cycle. These data has allowed us to propose a transport mechanism of antibacterial peptides. [1]



Cryo-EM structure of the SbmA transporter (left panel). PELDOR analysis of SbmA dynamics (right panel)

References

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Molecular Machinery for Proteostasis

J. H. Torpey[1], B. A. Haynes[1], A. H. Camp[2] and R. L. Isaacson[1]

[1] Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London, SE1 1DB, U.K.; [2] Department of Biological Sciences, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts, 01075, U.S.A.

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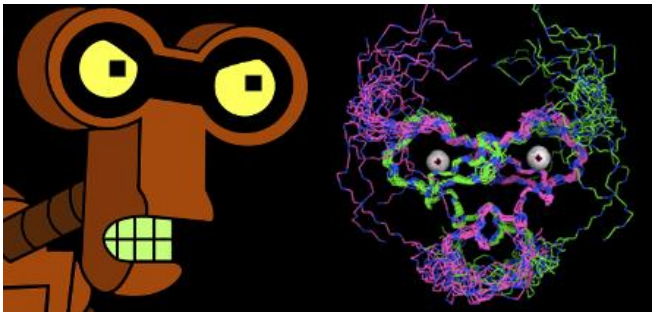

Animated journey through NMR structure determination for CsfB, a sporulation anti-sigma factor.

The crowded cell interior relies on many quality control mechanisms to ensure the correct protein machinery is present in the right places at the right times. I will present the latest results from two projects currently underway in our lab that unite within this theme. One investigates the temporal and spatial changes in protein content that facilitate spore-forming in bacteria as they wait out unfavourable environmental conditions[1]. The other explores triage of mislocalised hydrophobic proteins exposed to the aqueous cytoplasm of mammalian cells[2]. We use a range of biophysics techniques, including NMR, X-ray crystallography, cryo-electron microscopy, SAXS, EPR, native mass-spectrometry, modelling and more, to study structure, function and interactions of proteins involved in these processes.

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The effect of ethanol upon the function of respiratory complex I

J. Britton[1], J. Eisermann[1], J. Hindley[1], M. Devgan[1], O. Ces[1] and M. Roßler[1]

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Ethanol is one of the most widely consumed drug in the world, the average adult consumes in excess of 6 litres of ethanol per annum, leading to an estimated 2.8 million premature deaths. Excess ethanol consumption leads to a range of chronic health issues ranging from liver failure to cardiovascular diseases, significantly impacting the rate of respiration within exposed cells[1]. Ethanol can pass through membranes within 200 ns[2], enabling it to rapidly reach systemic exposure subsequent to absorption through the gastrointestinal tract.

Although consensus exists on the reduction of mitochondrial respiration upon exposure to ethanol, the effects of ethanol upon the individual components of the respiratory chain are as yet unclear[3]. We studied the effect of ethanol upon the largest protein within the respiratory chain, respiratory complex I (R-CI), which is essential for building the proton gradient used by ATP synthase. As well as investigating in its isolated state, R-CI was reconstituted into liposomes and ethosomes (see Figure 1) with its function characterised in each state by using previously published biochemical assays[4]. The alteration in the activity of R-CI with ethanol content was correlated with the changes in membrane viscosity and structure through further characterisation of membrane mimic with increasing ethanol. This was accomplished using EPR, x-ray scattering, solid state NMR and light scattering techniques.

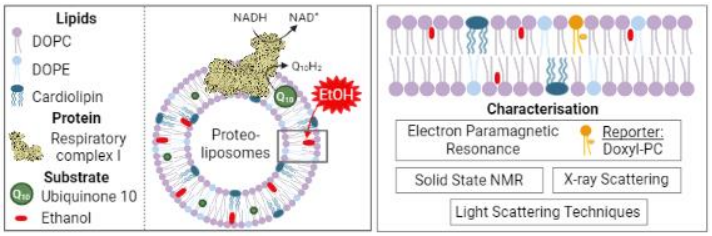

Figure 1: Effect of ethanol upon R-CI within self-assembled membrane systems. The lipid composition and other contents of the system are shown on the right.

References

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Inorganic Transmembrane 'Proteins'

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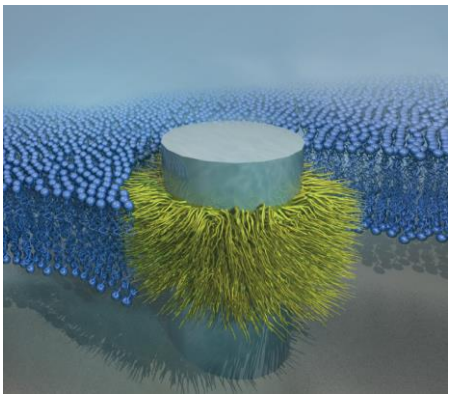

The ability to seamlessly integrate inorganic structures with biological membranes enables the possibility of merging the strengths of nanofabrication and nanotechnology with biological systems. This merging of inorganic and organic systems can enable new possibilities in areas ranging from cellular sensing to synthetic cellular systems. Here, I will discuss the use of bioinspired design principles to create nanofabricated transmembrane 'proteins' that feature 3-5nm hydrophobic bands for stable membrane integration. Past research has demonstrated that the molecular structure of the hydrophobic band plays a key role in the membrane-inorganic interface[1-3]. However, the molecular dynamics of the interface and the design rules on optimising the abiotic-biotic interface remain undetermined. The use of EPR presents an intriguing opportunity to shed light on this unique interface, in turn enabling new possibilities for merging nanofabricated structures with biological membranes.

References

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Redox-responsive, crosslinked polymeric nanogels for mRNA delivery

Rupali Dabas, Nazila Kamaly*

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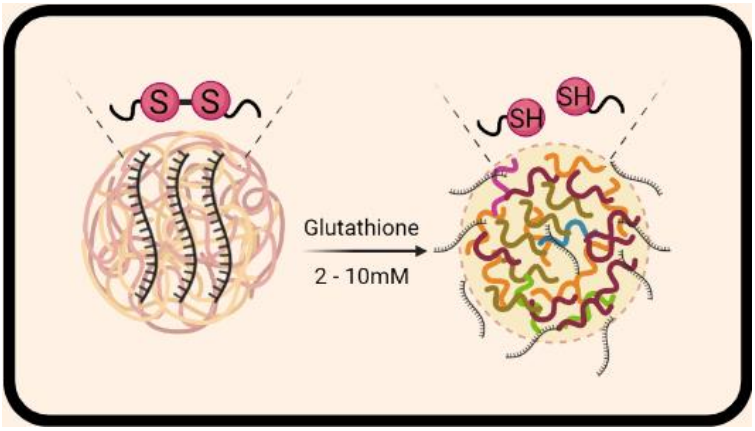

RNA therapeutics hold great promise for treating infectious diseases, cancer and genetic disorders. However, their inherent instability and large size pose formidable challenges that hinder their broad applications. There is a heightened interest in the development of safe and efficient vectors for RNA delivery in the clinical setting. Indeed, RNA-based nanotherapeutics have transformed the biomedical research landscape with their tremendous potential for highly specific disease intervention at the genetic level, and some have received FDA approval for clinical use, including the recent COVID-19 vaccines. To date, this field has been largely dominated by lipid-based systems, however, the design of lipid-based nanoparticles offers limited engineerability, for instance, in mediating controlled release of nucleic acid payloads. In contrast, owing to their chemical versatility, polymeric nanoscale hydrogels, or nanogels, can be designed by combinatorial free-radical polymerisation-based synthesis of various ionisable, cationic or stimuli-responsive moieties to modulate efficient entrapment and subsequent spatiotemporally controlled release of mRNA, thereby enhancing *in vivo* efficacy. By the inclusion of a glutathione cleavable crosslinker, we demonstrate nanogel-mediated delivery and subsequent redox-responsive release of mRNA payload in diverse cell types, thereby highlighting the promise of such nanogels as a novel construct for enhancing gene delivery with immediate value in clinical research.

Elucidating Copper Active Sites in Biology with Advanced EPR Spectroscopies

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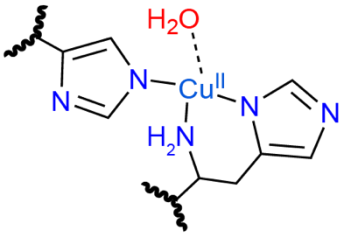
Lytic polysaccharide monooxygenases (LPMOs)[1] form a wide class of monocopper enzymes that break down lignocellulose material via oxidative cleavage at the glycosidic bond. All LPMOs have a distinct and well-recognizable monocopper active site, composed of only two histidine amino acids, forming what is commonly referred to as the 'His-brace.'



'His-brace' of LPMOs

The resting-state Cu(II) LPMO structure is often characterized by EPR spectroscopy due to the technique's high sensitivity to the copper's electronic structure. However, despite the common active-site among all LPMOs, diverse EPR signals are observed due to influences of other coordinating ligands (i.e. waters). Flexibility in this His-brace has been previously observed, and the role of the unique N-terminus amine ligand in catalysis are unknown.[2]

In my talk, I will discuss our work on deciphering the various copper EPR responses one may observe and their electronic and structural origins. Advanced pulsed hyperfine techniques, such as electron nuclear double resonance spectroscopy, yield more insight into the various ligands. Through a combination of advanced EPR spectroscopies, isotopic labelling, and DFT computations, we are building a complete picture of the LPMO copper active-site.

References

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Probing a key semiquinone intermediate in the mechanism of respiratory complex I with EPR spectroscopy

Eleanor Clifford[1], John J. Wright[2], Alberto Collauto[1], Judy Hirst[2], Maxie M. Roessler[1]

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Respiratory complex I (R-CI) couples NADH oxidation and ubiquinone-10 (Q_{10}) reduction to proton pumping across the inner mitochondrial membrane. A semiquinone (SQ) intermediate formed during Q_{10} reduction has been suggested to be key to this coupling mechanism and there have been several reports of such a g ~ 2 species observed using continuous wave (CW) EPR spectroscopy.[1] However, unambiguous assignment of observed EPR signals to a R-CI SQ has yet to be achieved.[2] Here, a synthetic membrane system and a highly sensitive EPR set-up using a cryogenic low-noise preamplifier[3] are employed to selectively investigate an organic radical species generated during R-CI catalysis (Fig. 1). CW EPR measurements reveal the presence of a piericidin A (R-CI inhibitor) sensitive radical signal at g ~ 2. To ascertain whether this signal can be attributed to a R-CI SQ, the properties, environment and location of the radical is probed using pulsed EPR techniques. Besides aiming to resolve a key step in the mechanism of R-CI, this work showcases how pulsed EPR may be used to investigate a g ~ 2 species that cannot be pinpointed using CW EPR alone.

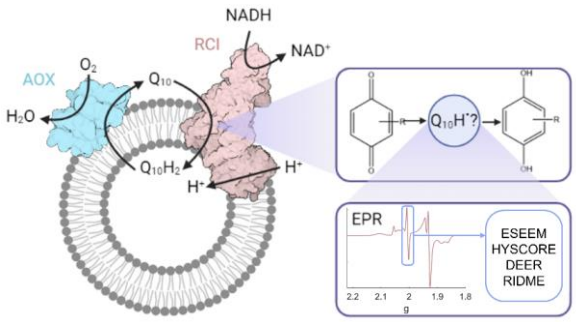

Figure 1: EPR is used to investigate the properties and environment of a g ~ 2 species generated under sustained R-CI turnover

References

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From Exploiting Paramagnetic [4Fe-4S] cluster to VITAS, a journey to antiviral natural product discovery

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I will present my journey from exploiting the paramagnetic iron-sulfur cluster to discovering and applying enzymes in antiviral synthesis. We used the paramagnetic properties of the [4Fe-4S] cluster of the antiviral enzyme S-adenosylmethionine (SAM)-dependent nucleotide dehydratase (also known as RSAD2)[1] to understand the chemistry[2]. This work led to the discovery of a new family of uncharacterized microbial enzymes predicted to produce antiviral nucleotide analogues[2] (one of the largest groups of FDA-approved antiviral drugs). To facilitate the discovery of new enzymes and engineer existing enzymes, we have recently developed an *in vivo* selection assay named VITAS (Figure 1B)[3].

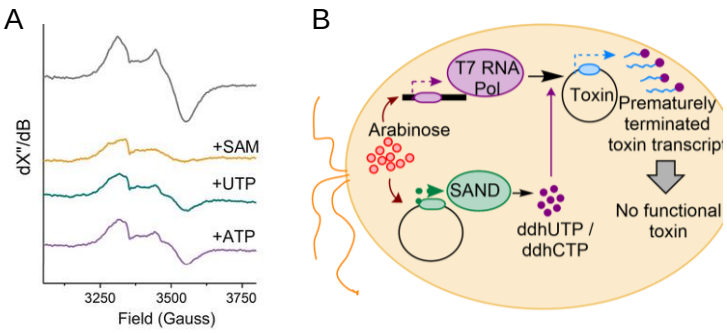

Figure 1. (A) Exploiting paramagnetic [4Fe-4S] cluster helped discover a new class of microbial enzymes producing new antivirals. (B) Principle of VITAS assay to discover antiviral natural products.

References

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Electronic structure and bonding in heterometallic clusters inspired by the C-cluster of carbon monoxide dehydrogenase

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Carbon monoxide dehydrogenases (CODHs) catalyze the reversible conversion of CO_2 to CO. The anaerobic variants of the enzyme contain an asymmetric [4Fe-1Ni-4S] cluster, known as the C-cluster. Three redox states of the C-cluster have been spectroscopically characterized: an inactive, fully oxidized form (C_{ox}); an active $S = 1/2$ reduced state (C_{red1}); and a further $2e^-$ reduced C_{red2} state. While the solid-state structure of some of these states has been reported, the electron distribution in the reduced states is unclear and spectroscopic evidence convolutes the picture. Inspired by the biological cofactor, we have prepared a synthetic [W-2Fe-Ni] cuboidal cluster with a structure that resembles the core [3FeNi] of the Cred states, i.e. featuring a three coordinate Ni site within a distorted cubane. EPR, Mössbauer, SQUID, and XAS data indicate that the best model is a surprising Ni^{1+} center alongside $2Fe^{2.5+}$ and W^{3+} , in which the unusual oxidation states are stabilized through significant metal-metal interactions. The electronic structure of this cluster and its oxidized form are discussed.

Characterization of a Porphyrin Iron(III) π-Dication

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Inspired by the enzyme Chloroperoxidase, inorganic chemists have sought to perform the oxidative umpolung of chloride by reacting it with Compound I.[1] However, in contrast to the enzyme, which forms an iron(III) hypochlorite, simple *meso*-substituted porphyrins generate a *meso*-chloro-isoporphyrin.[1,2] The key intermediate to the formation of this isoporphyrin is an iron(III) π-dication (Figure 1),[1,3] which are rare species in the literature for which limited characterization is reported.[3,4] We have recently identified a novel iron(III) π-dication bearing the tetraphenylporphyrin ligand and characterize it by ^{2}H-NMR, EPR, applied field Mössbauer, resonance Raman spectroscopy, and mass spectrometry.[5] In addition, we perform a computational study investigating the possible conformations of the porphyrin ring and the consequences that these have on the electronic structure.[5]

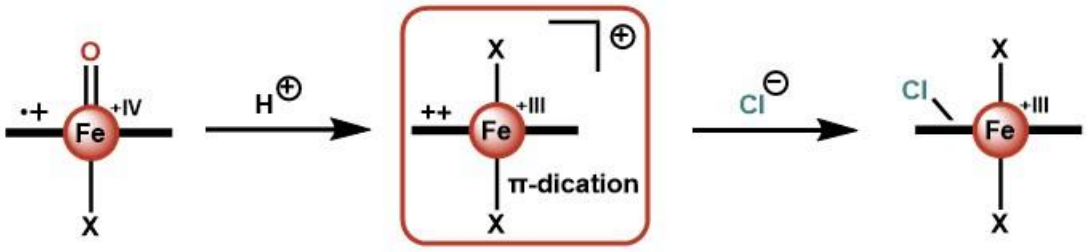

Figure 1. *Formation of an isoporphyrin, proceeding via an iron(III) π-dication.*

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Direct comparison of Light Induced Triplet-Triplet Electron Resonance (LITTER) spectroscopy with Förster Resonance Energy Transfer (FRET)

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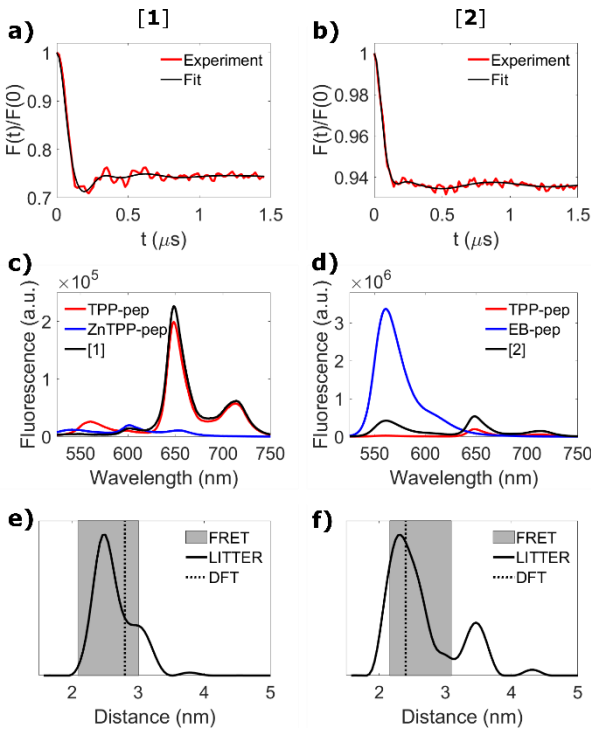

*Figure 1 - (a, b): 2-colour LITTER traces of 40 μM [**1**] (512/556 nm) and 40 μM [**2**] (512/532 nm) (red), respectively, with fits obtained by Tikhonov regularization (black). (c, d): Fluorescence spectra of [**1**] (c) and [**2**] (d) (black), and of mono-labelled TPP-peptide [**3**] (red), ZnTPP-peptide [**4**] (c, blue) and EB-peptide [**5**] (d, blue). Excitation was performed at 510 nm. (e, f) The determined distances for [**1**] (e) and [**2**] (f) by FRET (grey), LITTER (solid line) and DFT (dotted line). FRET analysis was carried out at 561nm.*

We present a direct comparison of light induced triplet-triplet electron resonance (LITTER) spectroscopy[1] with Förster resonance energy transfer (FRET)[2] in two peptide-chain systems of known length, augmented with different chromophore pairs.

The exemplar systems utilised Zn-substituted tetraphenylporphyrin (ZnTPP) and tetraphenylporphyrin (TPP) ([1]), as well as TPP and erythrosine B (EB) ([2]).

The inter-chromophore distances obtained from LITTER and FRET experiments are in very good agreement, with FRET giving distance ranges of 21.7-31.8 Å for system [1] and 20.5-29.2 Å in system [2]. The corresponding LITTER distance distributions centred on 23 and 25 Å respectively.

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The importance of membrane constitution – Impact of cardiolipin and ethanol on membrane fluidity

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Biological membranes are dynamic, semi-permeable structures mainly formed from bilayers of amphiphilic phospholipid molecules, harbouring small hydrophobic components, such as vitamins, quinones and pigments. In addition, they can host a huge range of membrane proteins from small, peripherally bound proteins to integral multicomponent megaDalton complexes.[1] The structure and composition of the lipid molecules, impacting the overall membrane fluidity and ordering (see Figure 1) of the membrane of interest, modulate the structures and activities of proteins.[2] The presence of lipids undergoing long-range diffusion acts as a good indicator to probe membrane integrity. Moreover, lipid fluidity dictates resistance against external environmental influences such as oxidative stress.[3]

In our study, we focus on the impact of cardiolipin (CL, an important lipid component of the inner mitochondrial membrane) on membrane fluidity and the ordering of model lipid systems used for the reconstitution of enzymes such as respiratory complex I (R-CI).[4] By understanding the interplay of CL with phosphatidylcholine (PC) and phosphatidyl-ethanolamine (PE), we aim to unravel how exactly the presence of CL impacts the catalytic activity of R-CI. To characterise the membrane fluidity, we combine Electron Paramagnetic Resonance (EPR) with Nuclear Magnetic Resonance (NMR) spectroscopy and X-ray scattering. In addition, we can probe the influence of additives such as ethanol to uncouple changes in protein functioning due to alterations in either the lipid environment and/or the enzyme itself. With our approach, we plan to (1) further highlight the importance of membrane constitution and integrity as well as (2) present an experimental route on how to study complex model membrane systems.

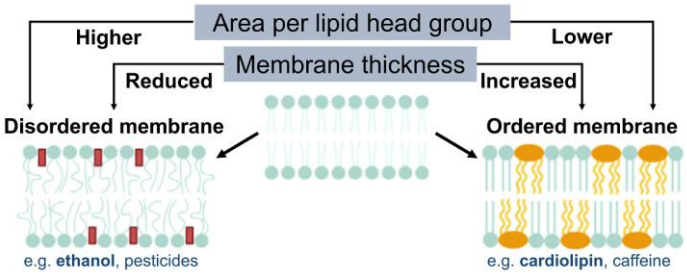

Figure 1: *Schematic representation of how different components inside a lipid bilayer can affect membrane ordering.*

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The interplay of ROS production and lipid peroxidation on respiratory complex I function

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Respiratory Complex I (R-CI) is an essential enzyme for the synthesis of ATP. It is also a major source of the production of reactive oxygen species (ROS) in mitochondria. Cardiolipin (CL), a phospholipid almost exclusively located in the inner mitochondrial membrane and essential for R-CI functioning, is especially prone to ROS attacks due to its high content of unsaturated fatty acids.[1] Alterations in the CL structure (due to oxidative stress) have been associated with mitochondrial dysfunction in several physio-pathological conditions such as ischemia. Although the mechanism of ROS production for isolated R-CI is relatively well understood[2], its effects on the surrounding membrane and downstream consequences on R-CI activity are unclear.

To study the interplay of R-CI functioning, ROS production and lipid peroxidation, we reconstituted R-CI into liposomes (see Figure 1).[3] These proteoliposomes enable the movement of ions and small radical species across the membrane to be investigated. We correlate changes in membrane fluidity with lipid peroxidation through the insertion of molecular rotors (synthetic organic fluorophores based on BODIPY-dyes) [4a] and spin-labelled phospholipids into the vesicles.[4b] Fluorescence and EPR spectroscopic characterizations are combined with biochemical assays to probe changes in the membrane morphology on the activity of R-CI.

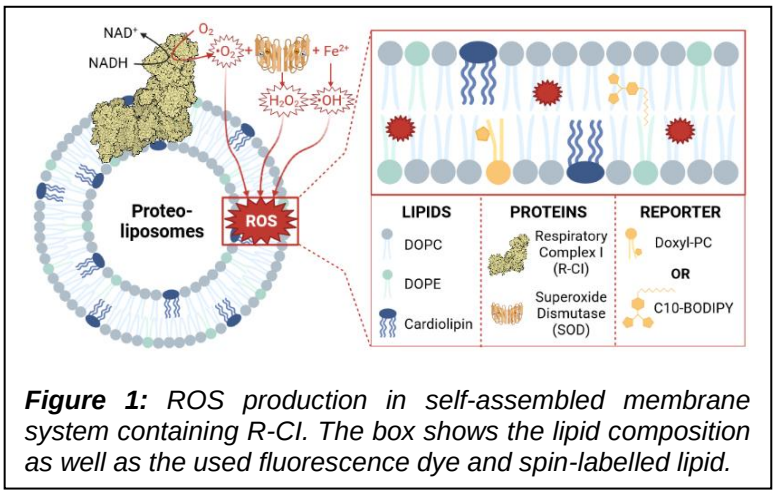

Figure 1: *ROS production in self-assembled membrane system containing R-CI. The box shows the lipid composition as well as the used fluorescence dye and spin-labelled lipid.*

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Purification and Characterisation of Hydrophobically Distinct Populations of Rubisco

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Ribulose-1,5-Carboxygenase/Oxygenase (Rubisco) is the enzyme responsible for the fixation of carbon in photosynthetic organisms. Previous work has shown that when purified by hydrophobic interaction chromatography Rubisco will elute in multiple fractions suggesting the existence of hydrophobically distinct populations[1]. This work aims to better characterise the cause of these populations by characterising Rubisco purified from *Arabidopsis thaliana* and mutant strains of *Chlamydomonas reinhardtii* that express hybrid Rubisco proteins.[2,3]

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Characterization of a Porphyrin Iron(III) π-Dication

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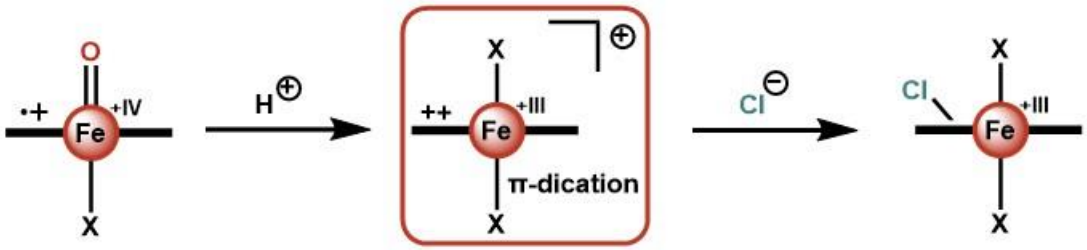
Inspired by the enzyme Chloroperoxidase, inorganic chemists have sought to perform the oxidative umpolung of chloride by reacting it with Compound I.[1] However, in contrast to the enzyme, which forms an iron(III) hypochlorite, simple *meso*-substituted porphyrins generate a *meso*-chloro-isoporphyrin.[1,2] The key intermediate to the formation of this isoporphyrin is an iron(III) π-dication (Figure 1),[1,3] which are rare species in the literature for which limited characterization is reported.[3,4] We have recently identified a novel iron(III) π-dication bearing the tetraphenylporphyrin ligand and characterize it by ^{2}H-NMR, EPR, applied field Mössbauer, resonance Raman spectroscopy, and mass spectrometry.[5] In addition, we perform a computational study investigating the possible conformations of the porphyrin ring and the consequences that these have on the electronic structure.[5]



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[5] S. Engbers, Y. Guo, J. E. M. N. Klein, *manuscript submitted*.

Ex-situ Protein Film Electrochemistry-Electron Paramagnetic Resonance (PFE-EPR): applications on the enzymatic complex "Methionine sulfoxide reductase QP" (MsrQP)

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The Methionine sulfoxide reductase Q (MsrQ) is an enzyme present in several gram-negative pathogenic bacteria. Together with its periplasmic partner, MsrP, this enzyme plays a vital role in repairing oxidative damages in the cell envelope. In the literature, it is suggested that electrons are transferred to MsrQ from the quinone pool, however no evidence of interaction with endogenous quinones is yet shown[1]. Additionally, it has been proved that MsrQ is the electron transfer partner of MsrP but the electron transfer mechanism between the subunits and their binding are not yet understood [2,3]. The PFE-EPR methodology developed in Roessler's group[4] is well suited for the investigation of electron transfer in this enzymatic complex. In this work, inner membrane vesicles (IMVs) with MsrQ overexpressed were isolated in order to obtain a sample with MsrQ in "in-vivo like" conditions. This allowed us to record an EPR spectrum of the MsrQ's heme in its natural environment which showed the presence of all the typical signals of a b-heme well described in the literature[3]. Quantification of these signals will provide information on the coordination of the cofactor and its orientation in the membrane. Furthermore, potentiometric titration combined to continuous wave (CW) and pulse EPR spectroscopy will help to characterize the interaction with natural quinones. In parallel to the IMVs route, custom made indium-tin oxide (ITO) electrodes coated with MsrP have been analysed with continuous wave EPR at different temperatures with the aim to characterize the interaction between the electrode and the protein. Preliminary results showed that the structure of the ITO seems to affect the relaxation processes of the molybdenum cofactor of MsrP without affecting the applicability of this protocol for the study of MsrQP. Next steps include the characterization of purified MsrQ on mesoporous ITO electrodes and the incorporation of MsrP on MsrQ-coated ITO electrodes to recreate the enzymatic system and describe the redox mechanism of the whole complex in full. Finally, immobilization of IMVs on ITO electrodes will allow to better understand the redox behaviour of the enzyme without the interference of redox mediators and will contribute to the characterization of the ITO effect on the paramagnetic centres.

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Polyaniline - bismuth ferrite Based Nanocomposite Immobilized on Liquid Natural Rubber as Integrated Adsorbents-Photocatalyst for Removal of Ciprofloxacin Antibiotic

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A hydrogel-based photocatalyst was employed to remove ciprofloxacin (CIP) from wastewater using a liquid natural rubber (LNR) / bismuth ferrite (BFO) hydrogel composite with incorporation of the chromophore, polyaniline (PANI), as a conductive polymer. Maleic anhydride (MaH) was added as the crosslinking agent while acrylic acid (AAc) enhanced the gelation process of the hydrogel composite. Response surface methodology (RSM) was used to optimize several parameters for the synthesis of the hydrogel composite and to monitor the adsorptive-photodegradation process. By monitoring the UV absorbance of CIP, without a post-treatment separation phase, the synthesized LNR-g-MaH/AA-PANI/BFO hydrogel composite showed astounding performance with up to 95% removal efficiency. The hydrogel composite was able to maintain extraction for up to ten cycles, indicating stability. Furthermore, CIP was adsorbed very rapidly under sunlight irradiation compared to removal under dark conditions, indicating that BFO and PANI caused photodegradation. Electron paramagnetic resonance (EPR) spectroscopy was used to monitor intrinsic paramagnetic centres during the photocatalysis. Further EPR-spin trapping experiments were used to identify reactive oxygen species generated during photolysis as evidence towards mechanism of action. The results show potential for the new hydrogel nanohybrid to improve the performance of wastewater treatment systems.

Electron Spins in Materials
From Catalysis to Quantum Phenomena

Oral contributions

EPR in catalysis	**M. Chiesa**	**EPR Approaches in Catalysis. A Personal View**
	L. Webster	Small molecule activation with titanium 'POCOP' pincer complexes
	M. Perez-Jimenez	A Paramagnetic Zn---Ni Hydride Complex: Synthesis, EPR Spectroscopy and Catalysis
	M. I. Parry	Polymer additives for the enhanced photodegradation of polyethylene
EPR in energy research	B. Ding	Imaging Key Electronic States in the Catalytic Reduction of Carbon Dioxide and Energy Storage using Electron Paramagnetic Resonance Spectroelectrochemistry
	Y. Dang	Film-electrochemical EPR: a new tool to investigate radicals in real time during redox processes
	J. Panidi	Improving Charge Carrier Properties of Organic Semiconductors for Thin Film Transistors
	T. Insinna	Graphite anodes for Li-ion batteries – an EPR investigation
EPR to investigate light-induced phenomena	**S. Richert**	**EPR of photogenerated spin systems for applications in materials science**
	J. Grüne	Quintet and Triplet Dynamics in Intramolecular Singlet Fission of Diphenylhexatriene Oligomers
	S. Gorgon	Ground state polarisation in a luminescent organic biradical
	H. Yang	Through-space and beyond: Characterisation of organic heterojunction model interfaces

Poster presentations

P1	Sara Belazregue	Towards iron pincer complexes for CO_2 hydrogenation
P2	Sarah F Chapman	Investigating the Surface Photodegradation of Agrochemicals
P3	J. Eisermann	Understanding non-covalent interactions in ionic liquids using EPR spectroscopy
P4	C. Parfitt	Synthesis & Reactivity of Chromium Pincer Complexes
P5	Molly I. Parry	Polymer additives for the enhanced photodegradation of polyethylene
P6	Fang Fang	Novel 'molecular wires' for long-distance electron transfer between the hierarchical electrode surfaces and redox-active molecules using Film Electrochemistry-EPR
P7	Jonathan Bar-David	Optical properties of the stable Blatter radical
P8	M. Di Girolamo	Chiral Induced Spin Selectivity Effect measured by means of Magnetic Conductive AFM
P9	L. Loci	Probing the Conformational Flexibility of Macromolecular Rotaxanes via Pulsed Electron Paramagnetic Resonance

EPR Approaches in Catalysis. A Personal View

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Understanding the electronic, chemical and structural properties of surface catalytic sites, their interaction with the surrounding matrix and their changes during a particular process is of paramount importance for the development of new catalytic systems, with maximized atom efficiencies, that are both versatile and robust for industrial manipulation. To this aim, increasingly intricate active sites are being designed and created, which deserve a meticulous understanding of their structure–property relationships. Among the vast arsenal of spectroscopic techniques used for interrogating heterogeneous catalysts, Electron Magnetic Resonance techniques can be of importance in obtaining a molecular level description of the structure and reactivity of paramagnetic species.[1,2] Such species, characterized by the presence of at least one unpaired electron, are frequently encountered in catalytic systems either as active species or catalytic intermediates and are often associated to transition metal ions (TMI). In this talk I will offer a personal view of potential EPR approaches related to heterogeneous and homogeneous catalysis, with emphasis on the application of hyperfine techniques.

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Small molecule activation with titanium ‘POCOP’ pincer complexes

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Pincer complexes have been widely applied with late transition metals and have shown to catalyse important chemical transformations, such as reversible CO_2 hydrogenation and C-H bond activation of arenes.[1,2] Despite the vast amount of research on pincer complexes, studies with early transition metals (group 4-6), especially containing ‘PCP’ type pincer ligands, is underdeveloped. A small number of groups have observed exciting reactivity of early transition metal pincer complexes, including methane activation and N_2 activation.[3,4]

We have recently published the synthesis of a range of ‘POCOP’ and ‘PCP’ type titanium pincer complexes and shown the capability of some of these complexes to activate dihydrogen.[5,6] This resulted in a rare titanium chlorohydride structure which has been and characterised by X-ray diffraction studies and EPR spectroscopy. This work explores the further reactivity of the titanium ‘POCOP’ complexes with other small molecules and monitoring these reactions by XRD and EPR studies.

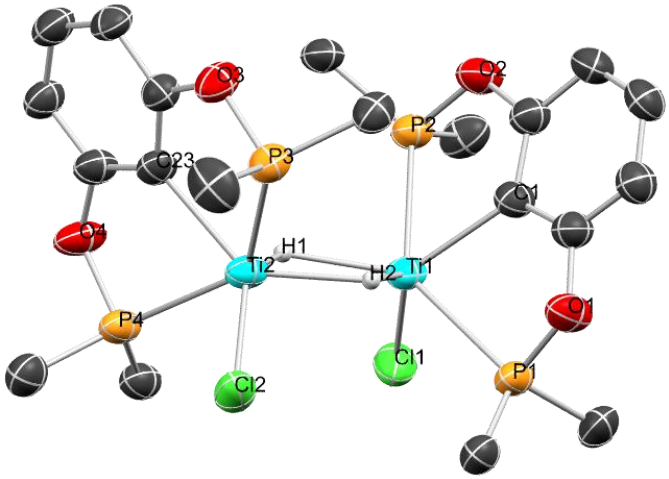

Figure 1: ORTEP plot of {(^{tBu}POCOP)Ti(μ-H)Cl}$_2$. Thermal ellipsoids at 50% probability, hydrogens (except bridging hydrides) and tert-butyl methyl groups omitted for clarity. Key: blue (titanium), red (oxygen), orange (phosphorus), green (chlorine), black (carbon), white (hydrogen).

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A Paramagnetic Zn---Ni Hydride Complex: Synthesis, EPR Spectroscopy and Catalysis

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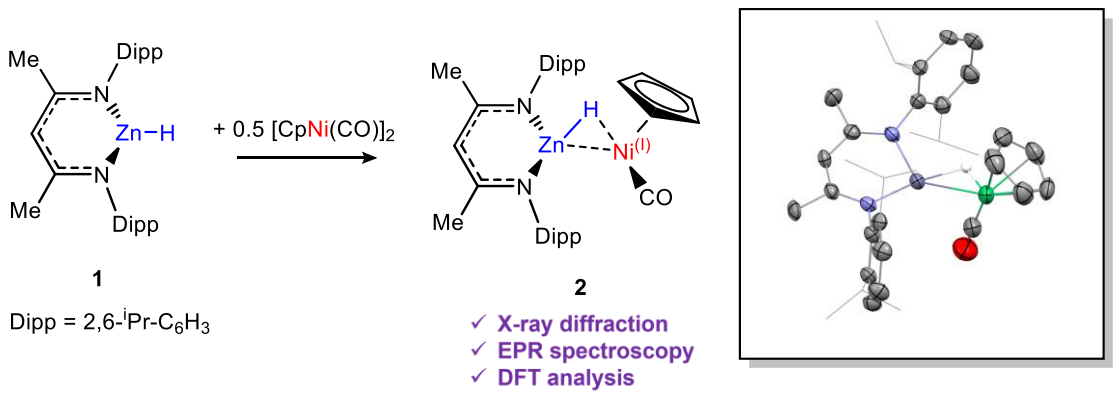
First-row metals are widely used by Nature for catalytic transformations.[1] For example, hydrogenase enzymes contain a recurrent motif in which two first-row metals are held in close proximity.[2] Understanding the bonding and reactivity of these types of motifs has the potential to unlock new insight and new catalytic applications. Herein, we present the reaction of zinc hydride **1** with a nickel(I) fragment, forming **2**. Compound **2** contains a hydride ligand bridging first-row Zn(II) and Ni(I) centres. Ni(I) hydride species have been proposed as key intermediates in catalytic transformations, but very few examples have been isolated and characterised.[3] Compound **2** is a paramagnetic 19-electron complex, exhibiting one unpaired electron.[4] It has been characterised by both X-ray diffraction and advanced EPR techniques (e.g. ENDOR, HyScore), as well as by computational methods.



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Polymer additives for the enhanced photodegradation of polyethylene

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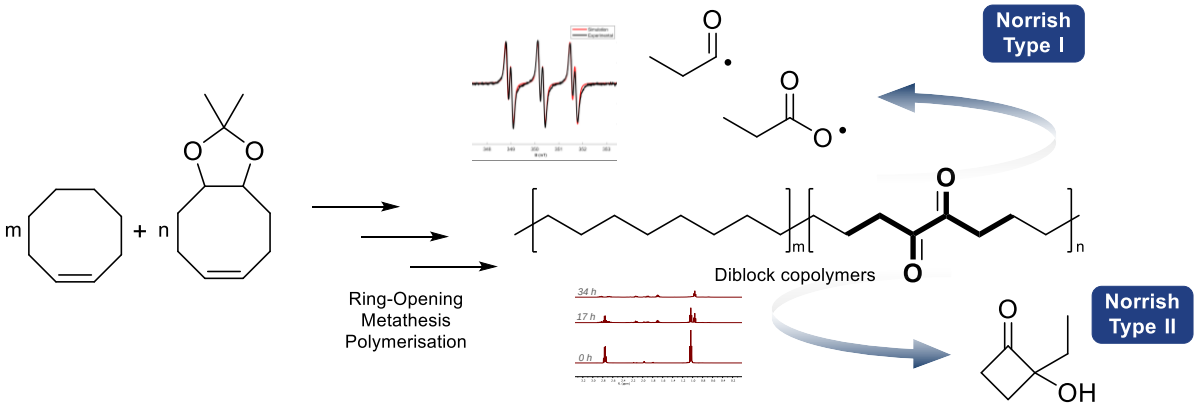
Polyethylene (PE) undergoes photodegradation due to the presence of intrinsic photoactive impurities. This is believed to occur via radical mechanisms, but mechanistic details are not thoroughly understood.[1] EPR can be used for the detection and characterisation of involved radical species.[2] A thorough understanding of the degradation process will aid in the design of alternative polymers, reducing their catastrophic environmental persistence.

Dicarbonyl-containing polyolefin analogues have been proposed as PE additives to enhance photodegradation. Here we discuss the synthesis of these additives, diblock copolymers consisting of a PE analogous region and region containing photodegradation target sites.[3] The photoreactivity of symmetric diketones, acting as models of these additives, is monitored. Reaction monitoring using *in situ* and *ex situ* irradiation, and NMR and EPR spectroscopies is used to understand mechanisms behind these photoreactions.



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Imaging Key Electronic States in the Catalytic Reduction of Carbon Dioxide and Energy Storage using Electron Paramagnetic Resonance Spectroelectrochemistry

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Understanding and exploiting the unique electronic states of each material is key to effectual application in both photo/electro-catalysis and energy storage, making electron paramagnetic resonance (EPR) crucial to investigations into newly developed materials for both fields. The coupling of EPR with electrochemistry, where EPR is performed in tandem with an applied potential resulting in *in situ* spectroelectrochemistry (SEC), further enriches its scope to image changing electron spins upon redox cycling, which is powerful in elucidating critical insights into charge transfer interactions, catalytic intermediates and stable charge storage states.

In this presentation, we discuss our development of a simple yet effective EPR SEC cell, that is constructed from readily available components and is compatible with solution, solid state, photo-activated and variable-temperature samples. This EPR SEC cell has been used to demonstrate the application of a cofacial naphthalenediimide-based metal-organic framework photocathode in the photoelectrochemical reduction of a Re-based CO_2 electrocatalyst to its catalytically active intermediate, enabling CO conversion with 78% Faradaic efficiency at markedly reduced overpotentials.[1] For squarephaneic tetraimide, a conjugated macrocycle for sodium-ion battery anodes, we also apply EPR SEC to confirm accessibility to a stable four-electron reduced triplet state that is Baird aromatic, empowering significant enhancements in material specific capacitance.[2]

EPR SEC cell

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Film-electrochemical EPR: a new tool to investigate radicals in real time during redox processes

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The combination of film electrochemistry (FE) and electron paramagnetic resonance (EPR) spectroscopy, FE-EPR, has attracted attention owing to its ability to monitor the redox behaviour of paramagnetic centres within a molecule of interest during both catalytic and non-catalytic reactions. The proof-of-principle has been established using mesoporous indium tin oxide (meso-ITO) as working electrodes (WE), but they still have disadvantages, namely a limited potential and pH range, fragility, and intrinsic EPR signal.[1]

To address these shortcomings, here, carbon nanotubes (CNTs) are used as an alternative. CNT buckypaper with high conductivity, high porosity and good robustness was made from reductively charged nanotubide solution,[2] and subsequently formed into electrodes. The optimised composition and geometry were determined and a typical nitroxide redox-spin label (a TEMPO derivative) was immobilised onto the buckypaper after electrochemical diazonium functionalisation. The FE-EPR CNT WE and the FE-EPR cell were designed and prepared (Fig. a), and the first example of in-situ FE-EPR measurements at room temperature was achieved using this set-up (Fig. b-d). Excellent consistency between the reduction potential of the nitroxide obtained from CV (0.812 V) and in-situ FE-EPR (0.806 V) demonstrated the compatibility of the CNT WE with FE-EPR and the direct, accurate potential control of this set-up. This work, therefore, not only demonstrates the feasibility of using CNT materials to extend the applications of FE-EPR beyond those possible with ITO, but also reveals its potential to investigate the mechanism of TEMPO catalysed alcohol oxidation.

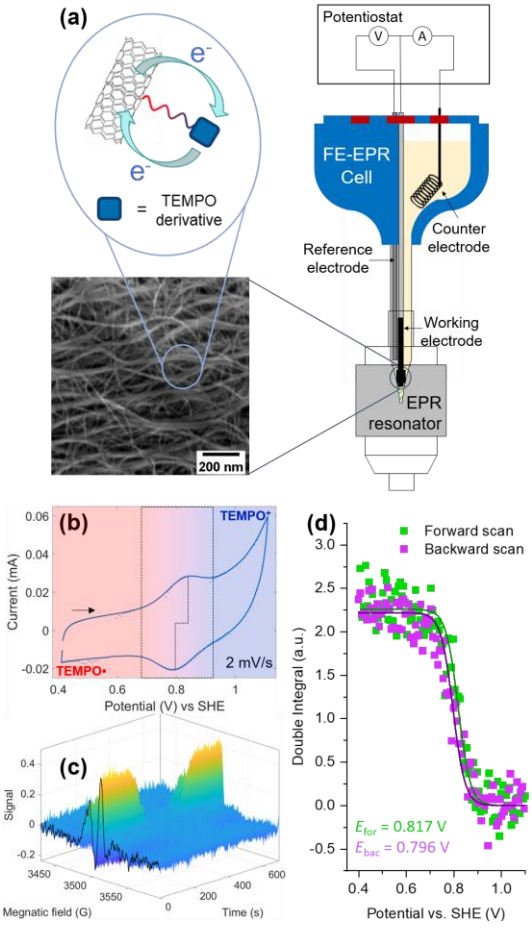

Fig: (a) Schematic of the in-situ FE-EPR set-up; (b&c) real-time CV-EPR measurement; (d) Nernst fitting curves revealing the transition between EPR-active TEMPO radical to its EPR-silent oxoammonium species TEMPO$^+$.

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Improving Charge Carrier Properties of Organic Semiconductors for Thin Film Transistors

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Due to the potential for low-cost manufacturing and the tunable properties of organic semiconductors are a promising option for optoelectronic applications. Improving their performance is a key requirement to enable faster commercialization. Charge carrier mobility is one crucial parameter for electronic applications and in particular for organic thin film transistors (OTFTs). A generic approach to achieve this is through the addition of molecular dopants in the organic semiconductor layer.

Here, we report the use of novel materials, as molecular dopants for both p[1,2] and n[3,4]-type organic semiconductors in OTFT devices. We show that key device parameters such as charge carrier mobility, contact resistance and threshold voltage improve dramatically upon the addition of the dopant. The effect of the dopant was analysed with Electron Paramagnetic Resonance (EPR) and by extracting the activation energy (EA) from low-temperature electrical characterisation. The impact of the dopant on the morphology of the OSCs will be also discussed as studied from Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD). Overall, this work highlights that controlled doping of organic semiconductor materials is the key to enhanced electronic devices.

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Graphite anodes for Li-ion batteries – an EPR investigation

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Graphite is a commercially successful anode for Li-ion batteries: its low cost, low toxicity and high abundance makes it ideally suited for batteries for devices, transportation and grid-based storage. The physical and electrochemical properties of graphite anodes have been thoroughly characterised, but one question remains unanswered—whether the electrons occupy localised states on Li or delocalised states on C, or an admixture therein. In this regard, electron paramagnetic resonance (EPR) spectroscopy is an invaluable tool for characterising the electronic states generated during electrochemical cycling. In this work, *ex situ* variable-temperature (10-300 K), variable-frequency (9-442 GHz) EPR was carried out to extract the *g*-tensors, linewidths, and metallicity of charged graphite at 4 different stages (from least to fully lithiated). We show that at high frequency (>300 GHz), the increased resolution offered by EPR enables up to three different axial environments to be observed, revealing heterogeneity within the graphite particles and the presence of hyperfine coupling to ^{7}Li. Importantly, our work demonstrates the power of EPR spectroscopy in investigating the local electronic structure of graphite on cycling, paving the way for this technique as a tool for screening and investigating novel materials for use in lithium-ion batteries.

EPR of photogenerated spin systems for applications in materials science

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Over the last decades, electron paramagnetic resonance (EPR) of photogenerated spin systems has found a wide range of applications in biology, chemistry, physics, and the materials science. Examples include the identification of key intermediates in photosynthesis, the study of triplet state spin delocalisation in molecular wires, the investigation of charge separation in organic photovoltaics, and the characterisation of triplet pair states in singlet fission materials.[1]

In the first half of the presentation, I will give a brief introduction to light-induced EPR spectroscopy and discuss the most common applications and experimental challenges. The second half will be devoted to our research in the field of molecular spintronics. After a short general overview, I will focus on photogenerated organic triplet–doublet systems, discuss their optical and magnetic properties, and illustrate their potential to be used as molecular spin qubit candidates for applications in the area of quantum sensing.[2–5]

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Quintet and Triplet Dynamics in Intramolecular Singlet Fission of Diphenylhexatriene Oligomers

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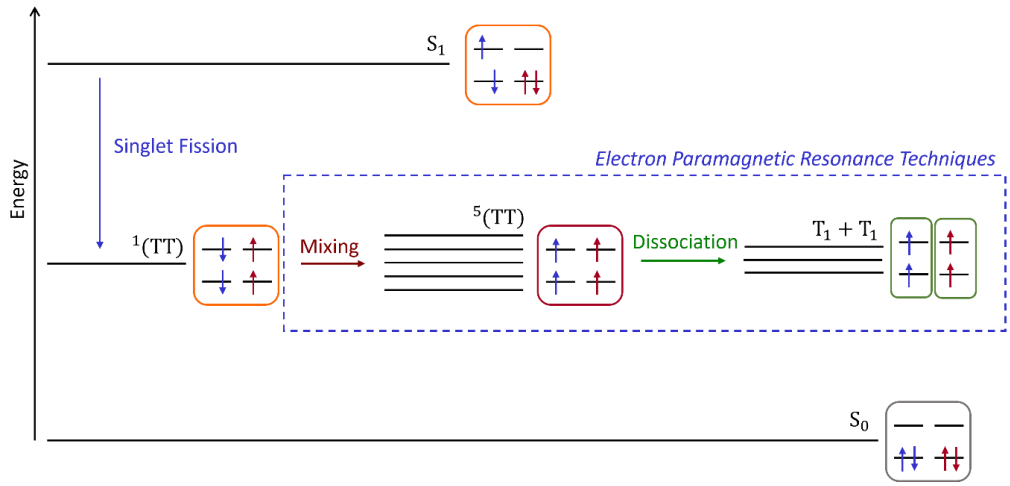
Singlet fission (SF) is a key concept for improving the efficiency of solar cells by enabling a multiplication of photoexcited states. The principle is based on a photoexcited singlet exciton rapidly decaying into spin-correlated triplet pairs that dissociate into free triplets. We combine the complementary techniques of optical spectroscopy with electron paramagnetic resonance (EPR) to monitor the intermediate states with different spin multiplicities. EPR spectroscopy thereby allows to indentify the involvement of exchange-coupled triplet pairs with quintet character (S=2), which dissociate into weakly coupled triplet pairs (S=1) via SF. We focus on new concepts of intramolecular singlet fission (iSF) based on units of the SF-active chromophore diphenylhexatriene (DPH). We found that upon fast iSF to generate strongly exchange-coupled triplet pairs, the efficiency of dissociation into free triplets strongly depends on the overall geometry and the number of molecular units. The characterization of various oligomers allows the study of the involved quintet and triplet dynamics to find a general recipe for efficient iSF materials.



Jablonski diagram of singlet fission (SF) process involving different spin-correlated triplet pair states.

Ground state polarisation in a luminescent organic biradical

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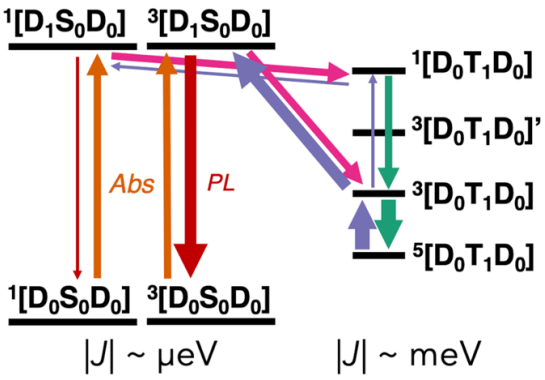
Robust spin-optical interfaces are key to harnessing the quantum resources of materials. However, organic candidates have been non-luminescent to date.[1] We have recently demonstrated molecules whose high-spin multiplicity excited states can efficiently access a luminescent state.[2] The mechanism we uncovered simultaneously supports pure initialisation, high fidelity of spin manipulations and light-based read-out at room temperature.

Here I will report an extension of this mechanism to a biradical. After light-induced quintet state formation, luminescence occurs preferentially through the triplet channel leading to long lived ground state polarisation observable in room temperature EPR. I will present the spin relaxation properties of excited and ground states of these luminescent mono- and bi-radicals in context of future applications.



State diagram of a luminescent biradical. Energy not to scale. The quintet can be thermally activated to a luminescent state.

The integration of luminescence and high-spin states creates an organic materials platform for new quantum technologies. Through the possibility of optical preparation of ground state polarisation, the biradical presents a tunable NV^- centre analogue.

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Through-space and beyond: Characterisation of organic heterojunction model interfaces

Hanbo Yang, Jeroen Royakkers, Flurin Eisner, Mohammed Azzouzi, Jarvist Moore Frost, Jenny Nelson, Hugo Bronstein

Control of the molecular configuration at the interface of an organic heterojunction is key to the development of efficient optoelectronic devices. Due to the difficulty in characterising these buried and (likely) disordered heterointerfaces, the interfacial structure in most systems remains a mystery. Here a novel model interface is synthesised by linking a donor polymer and non-fullerene acceptor ‘through space’. With the exact position and orientation of the moieties controlled, we investigated the excited state properties of the molecules and further showed that the kinetics of charge separation can be tuned with exciton size and delocalisation using transient absorption spectroscopy and transient EPR.

Towards iron pincer complexes for CO_2 hydrogenation

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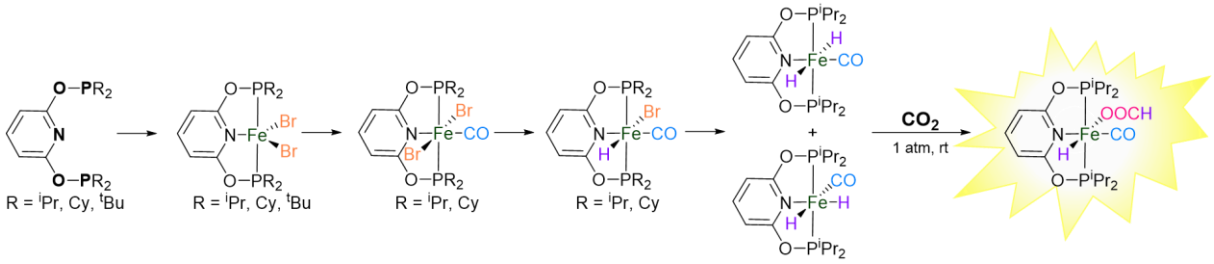
Demand for the catalytic hydrogenation of anthropogenic CO_2 to single carbon compounds is fast-growing, with the focus particularly on a homogeneous system employing an earth abundant transition metal like iron. Pincer ligands are renowned for their indispensable modularity, a useful feature in optimising these catalytic systems.[1] Transition metal complexes, such as Nozaki's Ir-PNP trihydride bearing a pincer ligand backbone, have been previously shown to activate the relatively inert CO_2 substrate, though pincer ligand fine-tuning is scarce.[2,3]



This work investigates the effect phosphinite-pincer backbone derivatisation has on the synthesis and reactivity of the corresponding iron 'PONOP' complexes. Novel cyclohexyl- PONOP Fe complexes have been synthesised. In targeting a suitable (PONOP)Fe precatalyst to the desired dihydride complex, hydride transfer reactions were found to be in competition with a solvent-dependent SET mechanism giving an Fe(I) species, as determined by EPR and NMR.[4] This undergoes a thermodynamically driven disproportionation to [(R-PONOP)Fe$(CO)_2$] (R = iPr, Cy).[5] The novel [(iPr-PONOP)Fe$(H)_2(CO)$] has also been synthesised *in situ* and shown to hydrogenate CO_2 to formate at mild conditions on NMR-scale.

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Investigating the Surface Photodegradation of Agrochemicals

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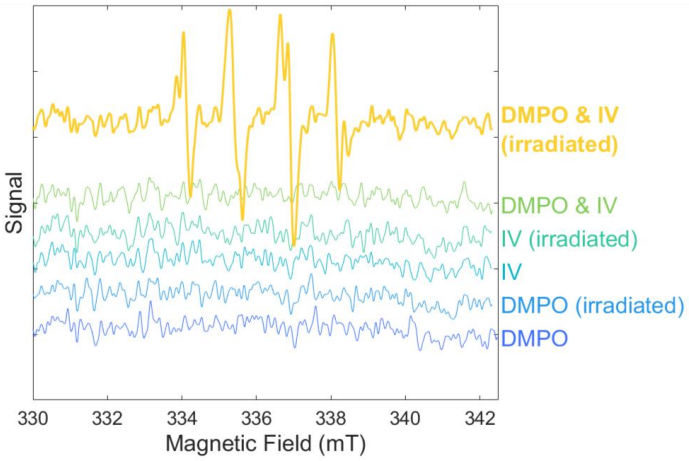
Significant population growth has caused a drive for more efficient crop production, meaning that more efficient agrochemicals are required to sustain the population.[1,2] Agrochemicals undergo photodegradation once they have been applied to the crop,[3] and an understanding of this can be exploited to develop more photostable, thus efficient, agrochemicals. In this study, novel methodologies were developed for analysis of agrochemicals and their photodegradation mechanisms on the leaf surface. The model agrochemical, Compound IV, was investigated using Electron Paramagnetic Resonance (EPR) and Liquid Chromatography-Mass Spectrometry (LC-MS) analyses. Spin trapping and scavenging techniques were used with EPR to determine whether a radical is formed on photoirradiation of Compound IV, and the kinetics of any formation that takes place. The spin trap used was 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), and the spin scavenger used was 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). A mimetic leaf surface was developed using enzyme extraction of ivy leaves to obtain the cuticular wax layer.[4] EPR analysis and optical microscopy was used to determine the suitability of this model for the investigation of radical intermediates on the leaf surface. Analytical results indicated that Compound IV photodegrades via a radical intermediate, short-lived species were formed upon irradiation of Compound IV with DMPO, and that a steady state in photo-initiated spin scavenging is reached after 20 minutes. It was also established that cuticular wax contains few intrinsic spins, making it suitable for EPR analysis. This work, therefore, laid the foundation to gain a better understanding of agrochemical photodegradation on the leaf surface.



Evidence that Compound IV photodegrades via a short-lived radical intermediate

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Understanding non-covalent interactions in ionic liquids using EPR spectroscopy

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Ionic Liquids (ILs) are a remarkable class of liquids, receiving huge attention for their potential in a range of applications such as synthesis and electrochemistry.[1,2] The most common ILs are composed of an inorganic anion with an organic amphiphilic cation and can segregate into ionic and non-polar domains. This nano-structure leads to different solvent environments for various solutes, with the combination of non-covalent interactions (e.g. coulombic interactions, hydrogen bonding, π-π interactions and dispersion interactions) known to be important.[3-4]

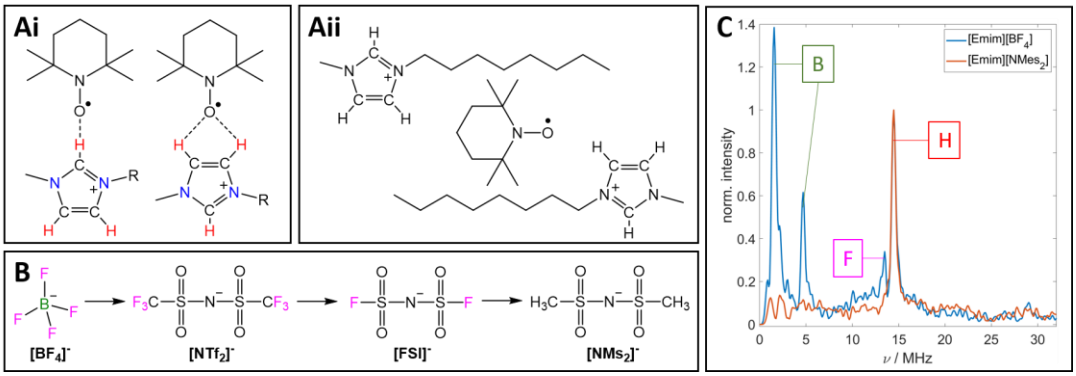

Figure 1: A – *Showcase of different possible interaction patterns between TEMPO as example amphiphilic radical species and an alkyl-imidazolium cation.* ***B –*** *Step-wise adjustment of the fluorine amount in the anion of the studied ILs.* ***C –*** *Example of X-band 3p-ESEEM nuclear frequency spectra of 4-Hydroxy-TEMPO (2 mM) in two 1-ethyl-3-methylimidazolium (Emim) ILs at 50 K.*

To probe how these interactions shape the macroscopic behaviour of solutes on a molecular level, we use TEMPO-based nitroxide spin probes to monitor the local environment in ILs containing alkyl-imidazolium cations with different counterions (Figure 1). The rotational mobility, proticity and hydrophobicity of the spin probes are investigated with CW EPR spectroscopy. To disentangle viscosity effects from specific interaction patterns induced by the IL, we compare them to water-glycerol mixtures with the same bulk viscosity. We further use pulsed EPR measurements to (1) determine the instantaneous diffusion of the spin probes and compare the derived local concentrations with their bulk concentrations, and (2) investigate the nuclei near the nitroxide radicals. These EPR measurements are providing the first insights into how the differences observed in the rotational dynamics are linked to the nanostructure inside ILs.

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Synthesis & Reactivity of Chromium Pincer Complexes

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The inherent modularity and tunability of pincer complexes has allowed chemists to use them to catalyse important and often challenging chemical reactions, including alkane dehydrogenation[1] and nitrogen fixation.[2] However, within this context, early transition metal (group 4-6) pincer complexes represent a very small and underdeveloped class of compound compared to their later counterparts.[3]

Our work has focused upon the deployment of these anionic pincer complexes using an alternative ligand precursor, featuring a lithium atom at the ipso-carbon position.[4] This approach, developed within the Chadwick group has facilitated the metalation of the so-called "*POCOP*" ligand, resulting in the formation of a high spin (***S*** = 3/2) paramagnetic complex, **1**. The electronic characteristics of complex **1** was probed using a variety of EPR spectroscopic techniques including continuous wave and pulsed techniques. This led to an extremely rare example of an observed coupling between a Cr(III) centre and a ^{31}P nuclei using pulsed EPR techniques.[5]

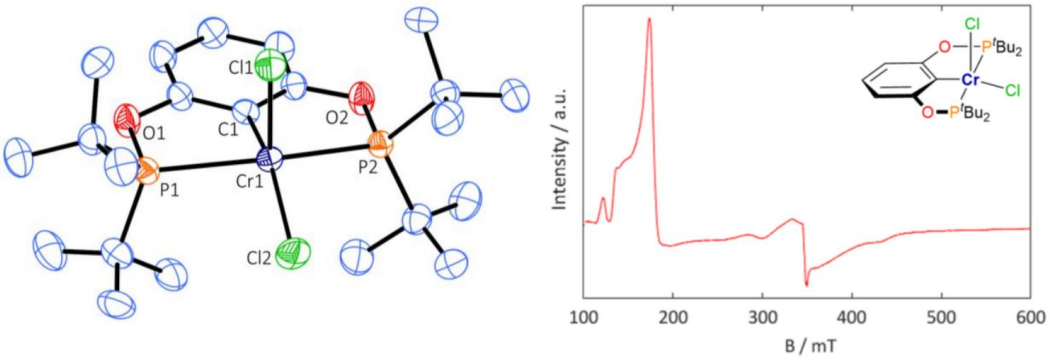

Figure 1. Left: *ORTEP plot of compex* ***1****.* ***Right:*** *X-Band CW EPR spectrum of complex* ***1*** *measured at 10 K.*

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Polymer additives for the enhanced photodegradation of polyethylene

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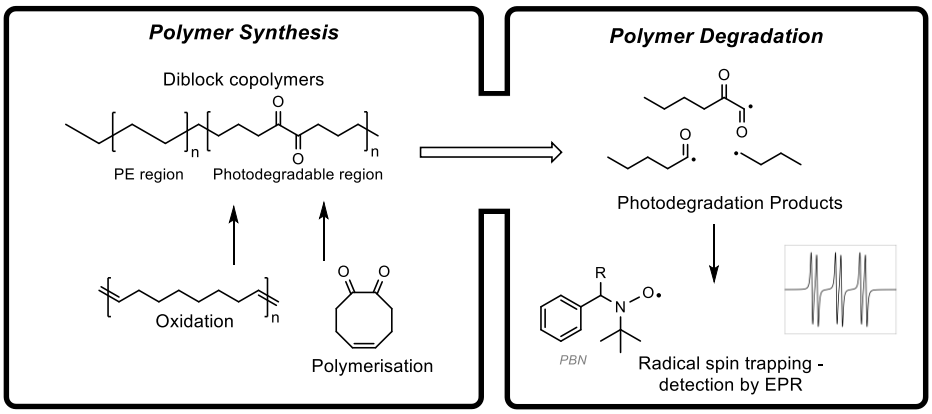
Whilst plastics have properties them attractive to countless applications, they are limited by their poor degradability and subsequent environmental persistence.[1] The intentional inclusion of photodegradation initiating carbonyl groups within polyethylene (PE) analogues gives long chain molecules that degrade upon irradiation.[2] Using these as additives within PE enhance photodegradability without compromising the properties.[3]

Here we discuss routes to potential carbonyl-containing PE additives.[4] Of particular interest are diblock copolymers consisting of a region containing diketone groups, and a subsequent region analogous to HDPE.[5] Additionally, the mechanisms behind PE photodegradation can be further understood using EPR spectroscopy. Spin trapping agents can be utilised to study the radical pathways that take place.



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Novel 'molecular wires' for long-distance electron transfer between the hierarchical electrode surfaces and redox-active molecules using Film Electrochemistry-EPR

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Film Electrochemistry (FE) is a transformative technique allowing real-time study of electrochemical reactions with picomolar quantities[1]. When coupled with EPR spectroscopy, FE-EPR can provide simultaneous information on both reactivity and the nature of key paramagnetic intermediates[2]. Because 3D porous electrode structures are required to achieve sufficient sensitivity, this necessitates new strategies to achieve effective long distance electron transfer between the electrode surface and the redox centre of interest. Here, a series of conductive molecular wires of different lengths were designed and synthetized. These are composed of three parts: an anchoring group, a conductive wire, and a binding group (Figure 1). As proof of concept, ferrocene was anchored at the end of the conductive wire and characterized by cyclic voltammetry and film electrochemistry-EPR.

The ferrocene with molecular wire was covalently attached onto indium-tin-oxide electrodes, and the dependence of the molecular wire length on conductivity was investigated. The results show that electron transfer is effective even over long distances (29.8 Å) in these hierarchical structures. EPR revels the presence of Fe(III) in the oxidised molecular wire. This work provides a foundation for anchoring complex proteins with buried redox centres onto hierarchical electrodes effectively, to enable combined protein film electrochemistry and EPR investigations.

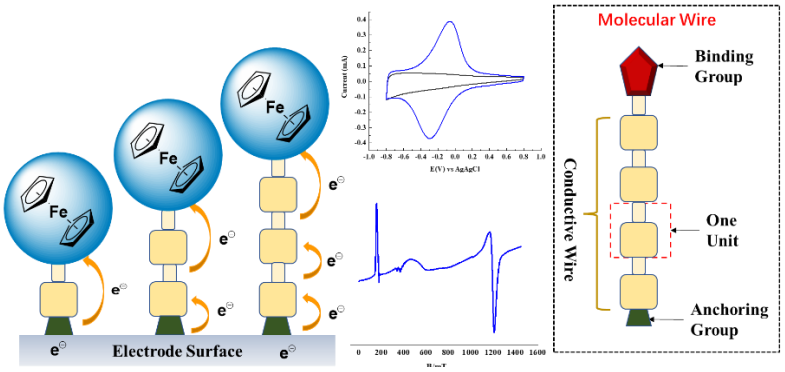

Figure 1: the concept of molecular wire

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Optical properties of the stable Blatter radical

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The 1,2,4-benzotriazin-4-yl[1] molecule (Fig.1A) is a thiolated variant of the Blatter radical[2], previously investigated for molecular electronics and energy applications[1]. We investigate the optical properties of this molecule when integrated into highly-confined optical cavities, as a potential marker for single-molecule ESR and as a two-level spin system[3] suitable for quantum technologies. Our aim is to form a chemical qubit, which can be interrogated by optically-detected magnetic resonance (ODMR)[4,5]. Emission and absorption measurements[6] reveal a HOMO-LUMO gap of 1.6eV, with significant photoluminescence (PL) in the visible and NIR (Fig. 1A). Additionally, cyclic voltammetry shows that the PL quenches with changes of the molecule oxidation state. When integrated into plasmonic nanocavities[7] (Fig. 1B) we form monolayers (SAMs) on the Au surfaces giving intense SERS and PL under laser excitation, and identifying the vibrational modes of the molecule ion the confined geometry.

These findings pave the way for optical detection of the magnetic resonance of these molecules at a single-molecule level.

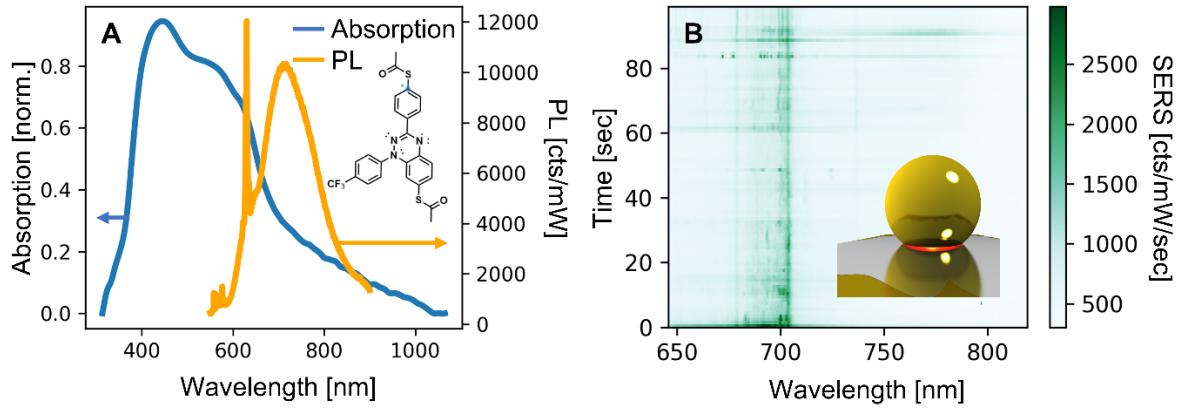

Figure 1. A) Absorption and PL spectra of Blatter radical in solution. B) Time-evolution of SERS/PL signal from Blatter radical in plasmonic geometry. Inset: NPoM geometry.

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Chiral Induced Spin Selectivity Effect measured by means of Magnetic Conductive AFM

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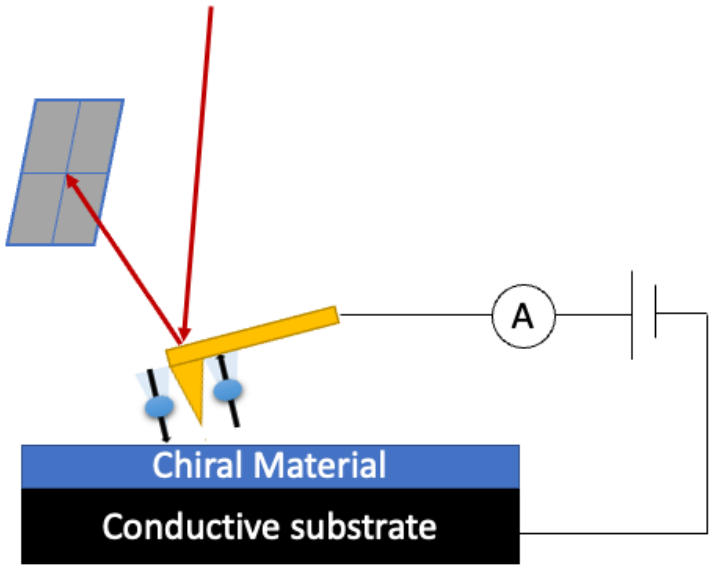
When an electron is transferred through a chiral molecule one spin is preferred over the other. This is the so-called chiral-induced spin selectivity (CISS) effect and it has attracted much attention in recent works for its several applications in molecular spintronics. [1] There are examples in the literature of the CISS effect measured by means of magnetic-conductive atomic force microscopy (mc-AFM). [2] In this work, the variables that affect the measurement have been thoroughly investigated and possible alternatives methods considered.



Magnetic conductive AFM measurement setup

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Probing the Conformational Flexibility of Macromolecular Rotaxanes via Pulsed Electron Paramagnetic Resonance

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Pulsed dipolar spectroscopy EPR techniques offer a deep insight into the nature of interactions between proximate electron spins.[1] Probing these spin-spin interactions enables the determination of interspin distances, and in some instances, the conformational flexibility of molecules via orientation selection.[2] Molecular Quantum Information Processing relies on well defined inter-spin interactions, and so characterising these interactions is vital for identifying suitable qubit systems.

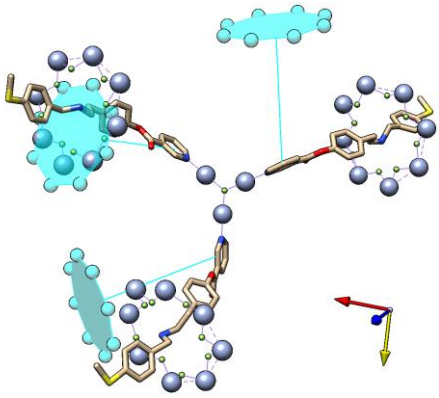

Figure *Crystal structure of one of the systems studied, overlaid with the most dominant solution-phase conformation (cyan octagons).*

By conducting and analysing orientation-selective 4-pulse Double Electron-Electron Resonance (DEER) measurements on a series of {Cr_7Ni} [4]rotaxane systems, measuring the inter-ring interactions, we determine that the conformational distribution of molecular geometries adopted by the systems in solution can differ considerably from those adopted in the crystal phase (see Figure for example). Structural comparison was achieved using a novel application of the Earth Mover's Distance analysis method.

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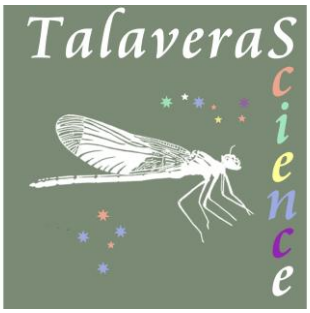
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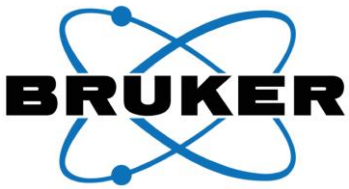
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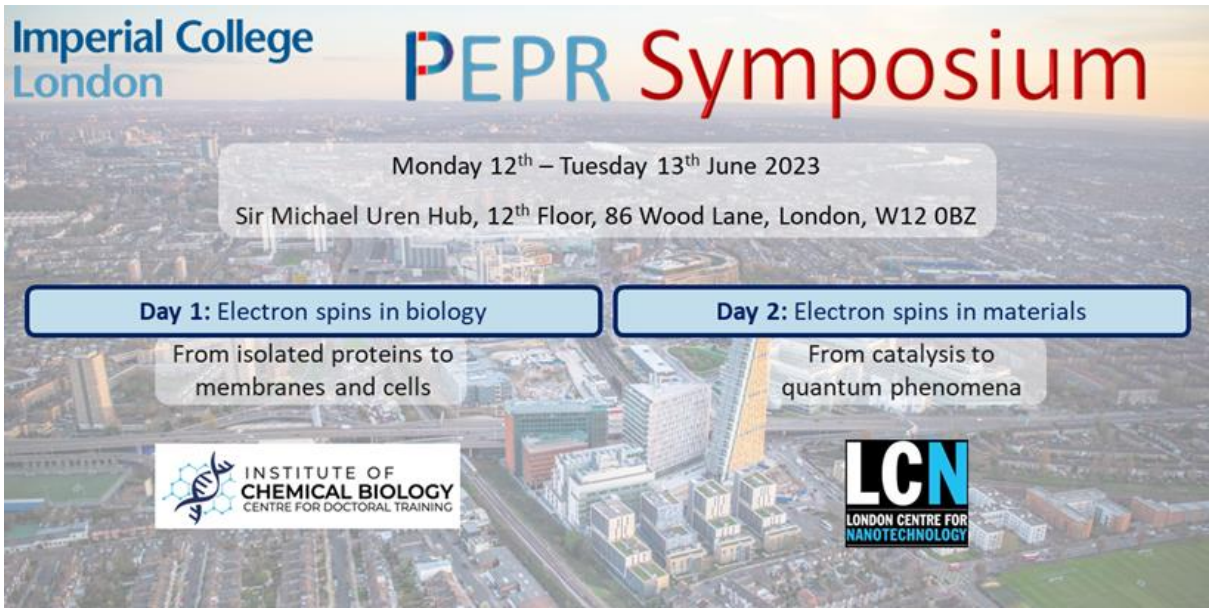
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