



The 54th Annual International Meeting
of the
ESR Spectroscopy Group
of the
Royal Society of Chemistry

12th – 16th April 2021

Virtual conference hosted by

University of Cardiff

Local Organiser: Dr Emma Richards

On behalf of the ESR Spectroscopy Group of the Royal Society of Chemistry, welcome to the 54th Annual International Meeting of the Group. For obvious reasons, this conference takes the format of being held fully online, hosted by Cardiff University. The scientific sessions are headlined by our plenary and invited speakers, and for younger researchers the JEOL Prize competition will run on Friday afternoon. We are especially grateful to the support provided by our generous sponsors of the meeting, who have supported various prizes.

We are also pleased to host the 35th and 36th Bruker Prizes, awarded to Profs David Collison and Michael Wasilewski respectively; and the 6th and 7th Bruker Thesis Prizes awarded to Drs Nabeel Aslam and Daphné Lubert-Perquel, respectively. We take this opportunity to offer our thanks (and commiserations!) to the Manchester Conference organising committee, which was unfortunately cancelled at the last hour in April 2020.

Despite the limitations of not being able to meet together in person, I hope you are able to engage fully in the conference programme and enjoy the excellent science presented by our community.

Emma Richards, *Local Organizer*

Plenary Speakers

Prof Emma Raven
University of Bristol

Prof Roberta Sessoli
University of Florence

Prof Josh Telser
Roosevelt University

Prof Stephen Hill
NHMFL, Florida State University

Invited Speakers

Prof Adrian Porch
University of Cardiff

Dr Sabine Richert
University of Freiburg

Dr Christos Pliotas
University of Leeds

Prof Bas de Bruin
University of Amsterdam

Dr Elizaveta Suturina
University of Bath

Prof Art van der Est
Brock University

ESR Spectroscopy Group Committee

Christiane Timmel (Chair)
University of Oxford, UK

Ilya Kuprov (Secretary)
University of Southampton, UK

David Norman (Treasurer)
University of Dundee, UK

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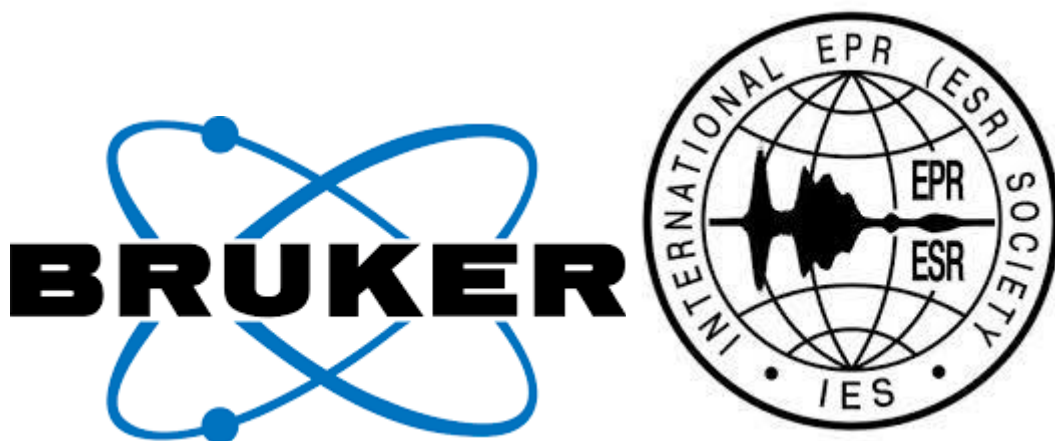
Florian Tuna
The University of Manchester, UK

Eric McInnes (2020 Organizer)
The University of Manchester, UK

Emma Richards (2021 Organizer)
Cardiff University, UK

Sponsors

We are grateful to the following sponsors for their generous support of various prizes.





The ESR Spectroscopy Group of the Royal Society of Chemistry is pleased to announce the 24th JEOL Prize Talk, sponsored by JEOL. The competition is open to any doctoral student (typically in year 2 or beyond) and 1st year postdoctoral scientists. The 15-minute lectures will be judged by the ESR Group Committee based on both scientific content and delivery. The competition is scheduled for Friday afternoon, with the winner announced via email and website press releases shortly after the close of the conference.

The following six lectures were selected by the committee, based on the abstracts submitted:

Nino Wili <i>ETH Zurich</i>	Dressing up electron spins to (un)lock their potential: Application to distance measurements between trityl radicals
Rajesh Patel <i>Warwick University</i>	Sub-nanotesla Magnetometry with a Fibre-Coupled Diamond Sensor
Joseph McPeak <i>Helmholtz-Zentrum Berlin für Materialien und Energie</i>	Highly Resolved Hyperfine Lines in Organic Radicals using Rapid-Scan Electron Paramagnetic Resonance
Samuel Jahn <i>University of Washington</i>	Electron Spin Decoherence In Deuterated Environments
Annalisa Pierro <i>Institute of Microbiology, CNRS</i>	Nitroxide-based SDSL-EPR for the study of protein dynamics in living cells
Katherine Richardson <i>Queen Mary Uni. London</i>	Functional basis of electron transport within photosynthetic complex I

Previous winners of the JEOL Student Prize

2002	Anna Ferretti	2008	Aleksei Volkov	2014	Daniel Klose
2003	Stefan Stoll	2009	Angelika Boeer	2015	Andrin Doll
2004	Dariusz Hinderberger	2010	Hans Moons	2016	Michael Lerch
2005	Malika Bouterfas	2011	Petra Lueders	2017	Jason Sidabras
2006	Janet Lovett	2012	Alice Bowen	2018	Leah Weiss
2007	Sharon Ruthstein	2013	Christopher Hartland	2019	Frauke Breitgoff
				2020	Gabriel Moise

Bruker Prize Lecture 2020



Prof David Collison

The University of Manchester

The 2020 Bruker Prize will be awarded to **Prof. David Collison** of The University of Manchester. The nominations emphasised David's seminal contributions to experimental and theoretical fundamentals of transition metal EPR, from bioinorganic chemistry to molecular materials, including his authoritative textbook. Crucially, they also stressed his important and selfless work in developing, supporting and nurturing the EPR community throughout his career. As co-founder and director of the successful EPSRC UK National EPR Facility, he has fostered collaboration not only between EPRists, but also between the EPR and wider science communities. This has had significant impact in widening the application base and popularising applications of EPR across the scientific spectrum.

Professor Collison will deliver the 2020 Bruker lecture entitled:

The attraction of unpaired electrons

The 2020 Bruker Prize lecture will be delivered live online at 1730 (BST) on Monday 12th April 2021.

Bruker Prize Lecture 2021



Professor Michael Wasielewski
Northwestern University

The ESR Spectroscopy Group of the Royal Society of Chemistry is pleased to announce that the 2021 Bruker Prize will be awarded to **Prof. Michael Wasielewski** of Northwestern University, for the development and application of Electron Paramagnetic Resonance to the study of photochemical and photophysical processes. Through his highly successful marriage of optical spectroscopy and EPR he has made pioneering contributions in the fields of artificial photosynthesis, nanoscale optoelectronics and quantum information science.

Professor Wasielewski will deliver the 2021 Bruker lecture entitled:

Exploiting Photogenerated Radical Pairs as Electron Spin Qubits for Quantum Information Applications

The 2021 Bruker Prize lecture will be delivered live online at 1730 (BST) on Tuesday 13th April 2021.

Bruker Thesis Prize 2020



Dr Nabeel Aslam

Harvard University

(Thesis completed at University of
Stuttgart)

The winner of the 2020 Bruker Thesis Prize competition was **Dr Nabeel Aslam** for his thesis completed at the University of Stuttgart, supervised by Prof. Jörg Wrachtrup.

Nabeel studied physics at the University of Mainz, Germany, and completed his studies in 2012. He then moved to Stuttgart, Germany, for his PhD in the institute of Prof. Jörg Wrachtrup. After earning his PhD degree in 2018, he joined the Department of Physics and Chemistry at Harvard University as a Postdoctoral fellow in the labs of Mikhail Lukin and Hongkun Park. He has been granted the Feodor Lynen fellowship by the Humboldt foundation.

Dr Nabeel will deliver the 2020 Bruker Thesis Prize lecture entitled:

Nanoscale NMR with a quantum sensor in diamond

The 2020 Bruker Thesis Prize lecture will be delivered live online at 1600 (BST) on Monday 12th April 2021.

Bruker Thesis Prize 2021



Dr Daphné Lubert-Perquel

*National High Magnetic Field
Laboratory*

(Thesis completed at Imperial College
London)

The ESR Group of the Royal Society of Chemistry and Bruker Corporation are pleased to announce the winner of the 7th Bruker ESR Thesis Prize is **Dr Daphné Lubert-Perquel** for her thesis "*Combining Film Design and Spectroscopic Strategies to Elucidate Triplet Dynamics in Molecular Systems*" completed at the Imperial College London, supervised by Prof Chris Kay and Prof. Sandrine Heutz.

As summarised by her thesis examiners "Daphne's thesis does justice to her exceptional talents as a researcher, and provides an outstanding narrative of the use of EPR spectroscopy to understand the photophysics of triplets in molecular systems... it makes a unique contribution to the field in terms of both its quality, and also its breadth [...]" In agreement with these observations, the RSC ESR assessors were impressed by the truly comprehensive approach Daphne took in tackling this project. From the design, synthesis and structural characterisation of the films to their investigation by EPR spectroscopy combined with complementary spectroscopic analyses and detailed calculations, the work of her thesis was an exciting scientific journey which elucidates the chemistry and physics of these exciting paramagnetic centres.

Dr Lubert-Perquel will deliver the 2021 Bruker Thesis Prize lecture entitled:

***Combining Film Design and Spectroscopic Strategies to
Elucidate Triplet Dynamics in Molecular Systems***

The 2021 Bruker Thesis Prize lecture will be delivered live online at 1600 (BST) on Tuesday 13th April 2021.



Previous winners of the Bruker Prize

1986	Martyn Symonds	1998	John Pilbrow	2010	Ronald Mason
1987	Klaus Möbius	1999	Jan Schmidt	2011	Thomas Prisner
1988	Hans Fischer	2000	Dante Gatteschi	2012	Kev Salikhov
1989	James Hyde	2001	Jürgen Hüttermann	2013	Takeji Takui
1990	Jack Freed	2002	Sandra and Gareth Eaton	2014	Jörg Wrachtrup
1991	E. de Boer	2003	Wolfgang Lubitz	2015	Robert Bittl
1992	George Feher	2004	Wayne Hubbell	2016	David Britt
1993	Neil Atherton	2005	Klaus-Peter Dinse	2017	Peter Höfer
1994	Arthur Schweiger	2006	Yuri Tsvetkov	2018	Sabine van Doorslaer
1995	Harden McConnell	2007	Daniella Goldfarb	2019	Marina Bennati
1996	Brian Hoffman	2008	Edgar Groenen		
1997	Keith McLauchlan	2009	Gunnar Jeschke		

Previous winners of the Bruker Thesis Prize

2015	Joshua Biller, University of Denver	2017	Andrin Doll, ETH Zürich	2019	Claire Motion, University of St Andrews
2016	Claudia Tait, University of Oxford	2018	Audrey Bienfait, CEA-Saclay		



International EPR Society Young Investigator Award



Dr Sabine Richert

Freiburg University

Dr Richert will deliver the 2020 International EPR Society Young Investigator Award lecture entitled:

***Exploring photogenerated molecular quartet states as
spin qubits***

**The 2021 IES YIA lecture will be delivered live online at 1440 (BST) on
Wednesday 14th April 2021.**

*The IES are also generously sponsoring two poster prize awards at this conference.

MONDAY 12th APRIL		
Session Chair: Damien Murphy		
14.00 – 14.10	Emma Richards Christiane Timmel	Conference Welcome
14.10 – 14.50 Plenary	Emma Raven University of Bristol	The role of heme in biology – from catalysis to regulation
14.50 – 15.00	Break	
Session Chair: tba		
15.00 – 15.40 Q&A Session	Sonia Chabbra	In situ EPR identification of active sites in FeNC catalysts for the oxygen reduction reaction and mechanism underlying Cr/PNP based ethylene tetramerisation catalysis
	Joyashish Debgupta	EPR Investigation of the Effect of Chemical Modification on the Charge Carrier Trapping in TiO ₂ Nanoparticles
	Claudia Tait	EPR characterisation of a doped organic semiconductor
	Marcus Giansiracusa	EPR verified metallocenate derivatives of Mn(I), Fe(I), Co(I)
	Michal Zalibera	Toward Visible Light-Activated Molecular Grippers
	Gunnar Jeschke	Ensemble modelling of intrinsically disordered protein domains with EPR-derived distance distributions: The case of hnRNP A1
	Hassane EL Mkami	High sensitivity Gd ³⁺ - Gd ³⁺ EPR distance measurements that eliminate artefacts seen at short distances
	Sergei Dzuba	The Structure of Lipid Rafts in Model Biological Membranes by DEER of Spin-Labeled Cholesterol Analog
	Hannah Russell	DEER and RIDME Measurements of the Nitroxide-Spin Labelled Copper-Bound Amine Oxidase Homodimer from <i>Arthrobacter Globiformis</i>
	Laura Galazzo	Nanodiscs or not nanodiscs? Conformational plasticity of an ABC exporter in different environments probed by EPR
15.50 – 16.10	Break	
16.10 – 16.20	Jörg Wrachtrup	Bruker Thesis Prize Laudatio
16.20 – 17.00 Bruker Thesis	Nabeel Aslam	Nanoscale NMR with a quantum sensor in diamond
17.00 – 17.20	Break	
17.20 – 17.30	Eric McInnes	Bruker Prize Laudatio
17.30 – 18.20 Bruker Prize	David Collison	The attraction of unpaired electrons

NB

Please see the website links in the table to access the pre-recorded videos for all ordinary talks. Note that these will remain hidden in the Youtube channel and cannot be found via search engine.

TUESDAY 13th APRIL		
Session Chair: tba		
14.00 – 14.10	Emma Richards	Session Welcome
14.10 – 14.50 Plenary	Roberta Sessoli <i>University of Florence</i>	Magnetic molecules in quantum nanoscience
14.50 – 15.00	Break	
Session Chair: tba		
15.00 – 15.40 Q&A session	Martina Huber	Determining Amyloid Oligomerization with Standard and High-Field EPR
	Bruno Guigliarelli	Probing H-bond Network Changes in Molybdenum Enzymes Through EPR Analysis of Intercenter Magnetic Coupling
	Alistair Fielding	Selective spin labelling of surface cysteines using a bromoacrylaldehyde spin label
	Maxie Roessler	Using a chimeric respiratory chain and EPR spectroscopy to determine the origin of semiquinone species previously assigned to mitochondrial complex I
	Juliane Stehle	Intracellular Protein-Lipid Interactions Studied by Rapid-Scan Electron Paramagnetic Resonance Spectroscopy
	Stephan Pribitzer	Determining electron–nucleus distances and Fermi contact couplings from ENDOR spectra
	Daniel Klose	Resolving small distance variations by single-molecule FRET & EPR spectroscopy using rotamer libraries
	Aharon Blank	The Potential of Pulsed Electron Spin Resonance for Tooth-based Retrospective Biodosimetry
	Michael Taylor	Investigating the elusive oxygen donor copper site within a protein type scaffold
	Rachel Haywood	Interaction between 694nm red (ruby) laser photons and a static magnetic field – artefact or evidence for photon charge and mass?
15.50 – 16.10	Break	
16.10 – 16.20	Stephen Hill	Bruker Thesis Prize Laudatio
16.20 – 17.00 Bruker Thesis	Daphné Lubert-Perquel	Combining Film Design and Spectroscopic Strategies to Elucidate Triplet Dynamics in Molecular Systems
17.00 – 17.20	Break	
17.20 – 17.30	Christiane Timmel	Bruker Prize Laudatio
17.30 – 18.20 Bruker Prize	Michael Wasielewski	Exploiting Photogenerated Radical Pairs as Electron Spin Qubits for Quantum Information Applications

WEDNESDAY 14th APRIL		
Session Chair: tba		
14.00 – 14.10	Emma Richards	Session Welcome
14.10 – 14.40 Invited	Adrian Porch <i>Cardiff University</i>	Microwave Cavities for Materials Characterisation
14.40 – 15.00 IES YIA Prize	Sabine Richert <i>Freiburg University</i>	Exploring photogenerated molecular quartet states as spin qubits
15.10 – 15.30	Break	
Session Chair: tba		
15.30 – 16.30 Q&A Session	Luis Fábregas Ibáñez	How do we separate a seemingly inseparable background?
	Ilya Kuprov	Training and reverse-engineering neural nets on EPR simulations
	Dima Svistunenko	Tyrosine and Tryptophan Radicals EPR Spectra Simulation - TRSSA on the EasySpin platform
	Thomas Schmidt	Two-Dimensional Reconstruction of Distance Distributions in Double Electron-Electron EPR Spectroscopy via Singular Value Decomposition
	Anna Matveeva	S/N additivity of Integral Mellin transfer as way to improvement of PDS experimental scheme
	Andriy Marko	Simulation of nitrogen nuclear spin magnetization of liquid solved nitroxides
	Andreas Gottscholl	Room Temperature Coherent Control of Spin Defects in hexagonal Boron Nitride
	Jannick Möser	Room-temperature formation of coherent spin pairs at silicon dangling bonds
	Matvey Fedin	Blatter Radical-Grafted Mesoporous Silica studied by EPR: Long Electron Relaxation Times and Opportunities for Spin Manipulation at Ambient Conditions
	Shang-Da Jiang	Quantum Phase Interference in a Fullerene-Based Electron Triplet Molecular Qutrit
	Arnau Bertran	Light-Induced Triplet-Triplet Electron Resonance Spectroscopy
	Michael Slota	Magnetic Edges and Coherence in Molecular Graphene Nanoribbons
16.30 – 16.50	Break	
Session Chair: tba		
16.50 – 17.20 Invited	Art van der Est <i>Brock University</i>	Spin Polarized Triplet States and Radical Pair States in Heliobacterial Reaction Centres
17.20 – 18.00 Plenary	Stephen Hill <i>NHMFL</i>	Controlling Electron-Nuclear Spin Couplings in Molecular Magnets

THURSDAY 15th APRIL		
Session Chair: tba		
14.00 – 14.10	Emma Richards	Session Welcome
14.10 – 14.40 Invited	Christos Pliotas University of Leeds	Using pulsed-EPR in the analysis of integral membrane proteins
14.40 – 15.10 Invited	Bas de Bruin Amsterdam University	Catalytic Metalloradical Reactivity of Carbenes & Nitrenes
15.10 – 15.30	Break	
Session Chair: tba		
15.30 – 16.30 Q&A Session	Graham Smith	Very High Sensitivity EPR – The HIPER upgrade
	Mantas Šimėnas	A sensitivity leap for X-band EPR using a probehead with a cryogenic preamplifier
	Oscar Kennedy	YBCO microresonators with ~50pL mode volume for high sensitivity EPR
	Silvio Küstner	Rapid Scan Electron Paramagnetic Resonance with EPR-on-a-Chip Sensors
	Lorenzo Tesi	High Frequency ESR: New Tools for Investigating Thin Layers of Molecular Magnets
	Markus Teucher	Milliwatt DEER on fast relaxing spin species
	Jean-Baptiste Verstraete	A chorus of chirps for broadband ESR spectroscopy
	Thomas Lohmiller	Accurate Determination of Exchange Interactions in Single-Chain Magnets and Other Multi-Spin Complexes by THz-EPR
	Sergey Tumanov	High-field EPR as a structural method for copper(II)-nitroxide magnetic compounds
	Sergey Veber	Easy-Plane to Easy-Axis Anisotropy Switching in a Co(II) Single-Ion Magnet Triggered by Diamagnetic Lattice
16.30 – 16.50	Break	
Session Chair: tba		
16.50 – 17.20 Invited	Elizaveta Suturina University of Bath	Role of magnetic anisotropy in paramagnetic relaxation enhancement
17.20 – 18.00 Plenary	Josh Telser Roosevelt University	EPR into the Almost Optical Region: Applications to Coordination Complexes

FRIDAY 16 th APRIL		
Session Chair: tba		
14.00 – 14.10	Emma Richards	Session Welcome
14.10 – 15.20	See abstract booklet	
Poster Session		
15.20 – 15.30	Break	
Session Chair: tba		
15.30 – 17.00 Jeol talks	Nino Wili <i>ETH Zurich</i>	Dressing up electron spins to (un)lock their potential: Application to distance measurements between trityl radicals
	Rajesh Patel <i>Warwick University</i>	Sub-nanotesla Magnetometry with a Fibre-Coupled Diamond Sensor
	Joseph McPeak <i>Helmholtz-Zentrum Berlin für Materialien und Energie</i>	Highly Resolved Hyperfine Lines in Organic Radicals using Rapid-Scan Electron Paramagnetic Resonance
	Samuel Jahn <i>University of Washington</i>	Electron Spin Decoherence In Deuterated Environments
	Annalisa Pierro <i>Institute of Microbiology, CNRS</i>	Nitroxide-based SDSL-EPR for the study of protein dynamics in living cells
	Katherine Richardson <i>Queen Mary Uni. London</i>	Functional basis of electron transport within photosynthetic complex I
17.00 – 17.10	Janet Lovett	2022 Conference Details
17.10 – 17.20	Emma Richards	2021 Conference Close



RSC ESR Annual Conference Cardiff
University
12 – 16th April
Paracat Satellite Meeting

Delegates must be registered for the main RSC ESR conference in order to access the Zoom sessions – see websites for further details.

RSC ESR Conference Website:

<http://www.esr-group.org/conferences/2021-conference-cardiff/registration-2021/>

Paracat Website:

<https://paracat.eu/wp/>

Monday	
12.00 – 12.15 Antonino Famulari	Structural insights into the heme domain of peroxxygenase-like cytochrome P450, CYP116B5hd
12.15 – 12.30 Andrea Guidetti	Development of a combined methodology towards mechanistic investigation of sustainable light-activated catalysts
Tuesday	
12.00 – 12.15 Seyedeh Fardokht Rezayi	An advanced EPR study to explore the Cu(I)- TREN complexes with trigonal bipyramidal structure
12.15 – 12.30 Paolo Cleto Bruzzese	Mapping Single-Metal Sites in Cu-CHA Zeolite with ¹⁷ O EPR: Structure and Dynamics
Wednesday	
12.00 – 12.15 Ilenia Serra	Arresting the Catalytic Arginine in Chlorite Dismutases: Impact on Heme Coordination, Thermal Stability, and Catalysis
12.15 – 12.30 Yu-Kai Liao	Chromium Environment in Cr-doped SAPO-5 from Spin Density Study
Thursday	
12.00 – 12.15 Maruan Bracci	Freeze quench: a practical approach
12.15 – 12.30 Leonora Podvorica	Multifrequency EPR investigation on isolated Ti(III) Species on the Surface of Pre-active Ziegler Natta Catalysts
Friday	
12.00 – 12.15 David Fioco	Photoactivation studies of Cr(I) complexes by EPR spectroscopy
12.15 – 12.30 Kavipriya Thangavel	EPR investigations on Cu(II) pairs in DUT-49(Cu) MOF to elucidate the magnetic coupling and Xenon adsorption properties

Nanoscale NMR with a quantum sensor in diamond

Nabeel Aslam,^{1,2} Matthias Pfender,¹ Philipp Neumann,¹ Rolf Reuter,¹ Andrea Zappe,¹ Felipe de Favaro Oliveira,¹ Andrej Denisenko,¹ Junichi Isoya³ and Joerg Wrachtrup¹

¹*Physikalisches Institut, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany.*

²*present address: Department of Physics and Chemistry, Harvard University, Cambridge, MA 02138, USA.*

³*Research Center for Knowledge Communities, University of Tsukuba, Tsukuba, 305-8550, Japan.*

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique, used for chemical structure analysis. Its low sensitivity, however, requires many identical molecules in the sample. Detecting single molecules with conventional NMR spectroscopy is therefore not feasible. This limitation can be overcome by utilizing optically addressable single electron spins in diamond: the nitrogen-vacancy (NV) centers. These quantum sensors have been used for the detection of nanometer-scale volumes of nuclear spins at ambient conditions [1]. Until recently the method was only able to differentiate between nuclear spin species. Chemical structure analysis via e.g., chemical shift detection was not possible due to insufficient spectral resolution. In the talk it will be shown how the spectral resolution of the NV nano NMR probe can be improved by three orders of magnitude (compared to previous studies). This results in the recording of chemical shift resolved ¹H and ¹⁹F NMR spectra of zeptoliter sized volumes [2]. Crucial for this result is the application of a magnetic field of up to 3 T. This comes with the challenge of combining a confocal microscope with electron spin manipulation at frequencies up to 90 GHz. Moreover, single nuclear spins have been integrated into the measurement sequence, as quantum memories, allowing phase acquisition times in the order of minutes.

[1] T. Staudacher, F. Shi, S. Pezzagna, J. Meijer, J. Du, C. A. Meriles, F. Reinhard, J. Wrachtrup, *Science*, 2013, 339, 557-560.

[2] N. Aslam, M. Pfender, P. Neumann, R. Reuter, A. Zappe, F. F. De Oliveira, A. Denisenko, H. Sumiya, S. Onoda, J. Isoya, J. Wrachtrup, *Science*, 2017, 357, 67.

The Attraction of Unpaired Electrons

David Collison, and very many collaborators

Department of Chemistry, and Photon Science Institute,

The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

david.collison@manchester.ac.uk

The audience for this talk does not need convincing that the world runs on unpaired electrons. It has become commonplace to find members of the family of EPR techniques reported in many of the journals devoted to science, technology, environment and medicine. It is a privilege to be in a position to support these types of research by hosting the National Research Facility (NRF) for EPR Spectroscopy, funded by EPSRC. Many of the projects in the NRF turn on the interactions between unpaired electrons, which can span over ten orders of magnitude in energy. The seminal work of Bleaney and Bowers [1] provided a platform to which those of us involved in studying multi-centred radicals continue to return, see Figure 1 (*left*). These interactions can provide an unexpected observation, or become a nuisance, or define the focus of ongoing research, see Figure 1 (*right*). [2] Using examples from our work in Manchester and beyond, which is supported by excellent synthetic chemists, this lecture will show how electron-electron interactions can be measured, manipulated and used to the benefit of a wide scientific community.

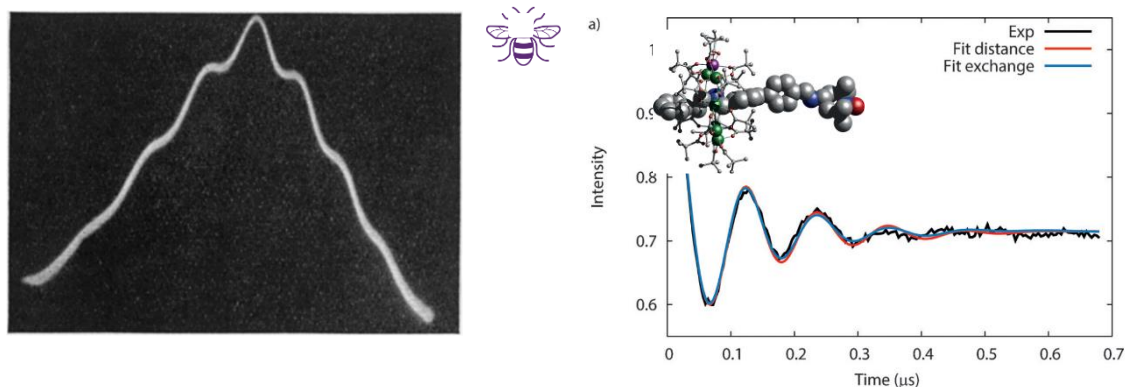


Figure 1. (*left*) Oscillogram showing hyperfine structure in “copper acetate”, [1] (*right*) RIDME traces measured on a hybrid [2]rotaxane, {[Ph-(CH₂)₂-NH₂-CH₂-(C₆H₄)₂-TEMPO][Cr₇NiF₈(O₂C^tBu)₁₆]}, at 33.8159 GHz and 1.2027 T as a frozen solution in toluene at 5 K. [2]

[1] B. Bleaney and K.D. Bowers, *Proc. Roy. Soc. Lond. A.*, 1952, **214**, 451-465.

[2] M.-E. Boulon, A. Fernandez, E. Moreno Pineda, N. F. Chilton, G. A. Timco, A. J. Fielding and R. E. P. Winpenney, *Angew. Chem. Int. Ed.*, 2017, **56**, 3876-3879.

Combining Film Design and Spectroscopic Strategies to Elucidate Triplet Dynamics in Molecular Systems

Daphné Lubert-Perquel¹, Enrico Salvadori², Anna Szumska³, Mohammed Azzouzi³, Dongkuk Kim¹, Stoichko Dimitrov⁴, Jenny Nelson³, Christopher W. M. Kay⁵, Sandrine Heutz¹.

¹ *London Centre for Nanotechnology and Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, U.K.*

² *Department of Chemistry, University of Turin, Via Giuria 7, Turin 10125, Italy*

³ *Department of Physics, Imperial College London, Prince Consort Road, London SW7 2BP, U.K.*

⁴ *Department of Chemistry, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.*

⁵ *Department of Chemistry, University of Saarland, 66123 Saarbrücken, Germany*

Pentacene is a benchmark aromatic molecule due to its remarkable photophysical properties and here we show these can be tuned by the local microstructure. In this work, we present a thorough analysis of oriented pentacene thin films using electron paramagnetic resonance (EPR) spectroscopy complemented by optical spectroscopy and an array of characterisation techniques.[1-4] The molecular aggregation and configuration of diluted pentacene films is correlated to the two triplet population mechanisms, intersystem crossing (ISC) and singlet fission (SF).[1] Moreover, the differing dynamics of the exciton pathways is calculated from EPR spectra using kinetic modelling. The triplets generated by SF are strongly coupled and populate higher spin states, namely quintets. The dynamics were elucidated according to molecular geometry by combining experimental data with density functional theory calculations. The differences in kinetics are postulated to originate from variations in the coupling strengths and localisation of orbitals.[4] Understanding which configurations act as traps for the triplets provides invaluable insight for the optimisation of OPV device architecture.

This project is at the interface of spectroscopy - both magnetic and optical - and materials science, where EPR provides a bridge between multiple characterisation techniques. It is a central tool to understand the fundamental principles underlying OPV devices. The more complete portrait of the kinetics also provides design rules for future optoelectronic applications. The orientation control and identification of dynamics according to a chosen orientation will have repercussions in a broad range of fields within the EPR community. From nanotechnology and molecular magnetism to biochemistry, the principles developed in this work may be applied where decoupling the effect of geometry from the fundamental processes of photoinduced electron transfer could resolve some of their respective challenges.

[1] Lubert-Perquel, D., *et al.*, Nature Commun., 9, 4222, (2018).

[2] Lubert-Perquel, D., *et al.*, J. Mater. Chem. C., 7, 289, (2019).

[3] Kim, D., *et al.*, Mater. Horiz., 7, 289, (2020).

[4] Lubert-Perquel, D., *et al.*, J. Phys. Chem. Lett., 11, 9557, (2020).

Exploiting Photogenerated Radical Pairs as Electron Spin Qubits for Quantum Information Applications

Michael R. Wasielewski

Department of Chemistry and Center for Molecular Quantum Transduction
Northwestern University, Evanston, IL 60208 USA

Ultrafast photo-driven electron transfer reactions are used to prepare entangled electron spin pairs having a pure initial spin state, an essential criterion for their use as spin qubit pairs (SQPs) in quantum information applications. For example, we have achieved electron spin state quantum teleportation in an ensemble of covalent donor-acceptor-stable radical molecules (Fig. 1A). In addition, we have extended this work to encompass photogenerated SQPs in synthetic DNA hairpins, which provide new opportunities for creating scalable qubit assemblies (Fig. 1B). We have also shown that photoexcitation of CdSe/CdS core/shell quantum dots covalently linked to electron acceptors can be used to generate highly spin polarized SQPs (Fig. 1C). In addition, we have demonstrated a two-qubit controlled-NOT (CNOT) gate (Fig. 1D) which is necessary for developing a complete set of universal quantum logic gates. These results show that photo-driven electron transfer processes in molecular systems provide an excellent means to understand and manipulate quantum information.

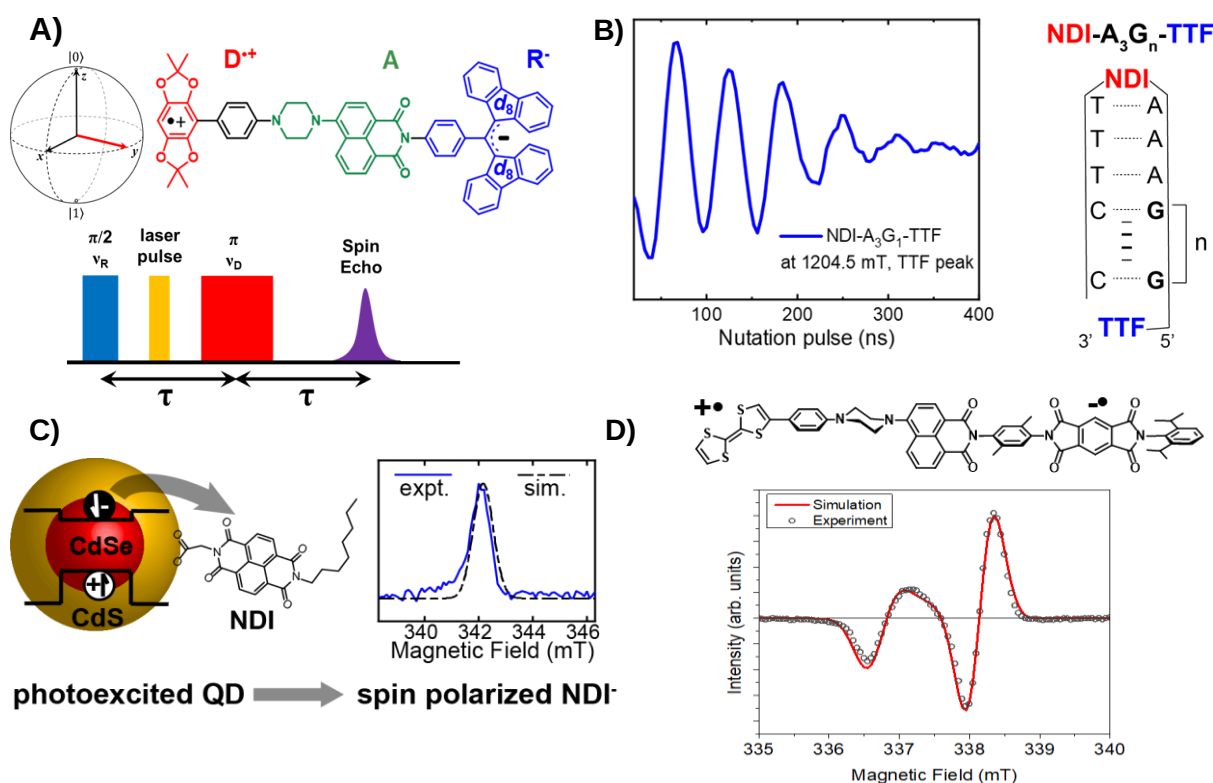


Fig. 1. A) Electron spin teleportation; B) Spin qubit pair coherence in DNA; C) Spin polarization using quantum dots; D) CNOT gate using a photogenerated spin qubit pair.

The role of heme in biology – from catalysis to regulation

Emma Raven

School of Chemistry, Cantock's Close, University of Bristol, Bristol BS8 1TS

The talk will explore the role of heme iron in biology, and will highlight the ways in which spectroscopic and crystallographic methods can be brought to bear on the question. It will start at the beginning with globins and cytochromes, and lead into catalytic enzymes and a discussion of their reactive intermediates. At the end, the talk will explore newer, regulatory roles for heme in larger and more complicated systems, and the possibilities that this offers for the future.

Magnetic molecules in quantum nanoscience

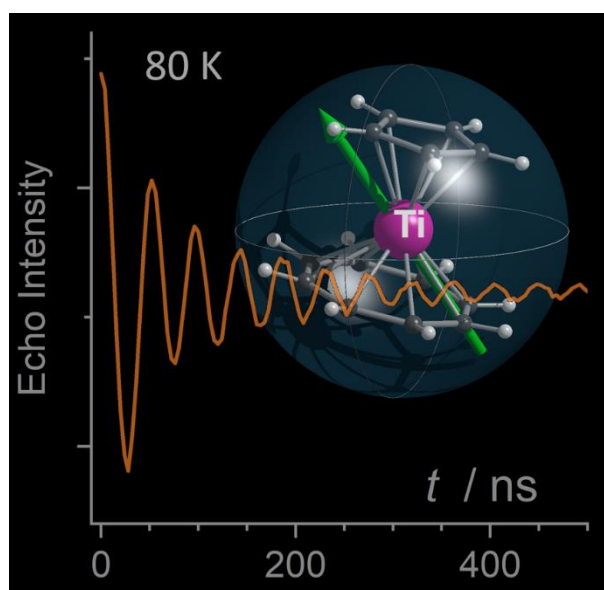
Roberta Sessoli

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Implementation of Quantum Technologies might benefit from the remarkable quantum properties shown by molecular spin systems. In the field of quantum information technology several physical realizations of the basic unit, or qubit, are currently investigated. Actually, the most advanced platform is constituted by superconducting circuits, but spin systems continue to attract interest as intrinsic highly coherent two-level systems, which can be easily manipulated by electromagnetic radiations.

Though molecules exhibit shorter spin coherence times than spin impurities in extended lattices, they have the advantage that they can be replicated in large quantities and their magnetic properties tuned through molecular synthetic strategies.^{1,2} They can be designed to host several qubits with a precise control of their interaction allowing for the realization of quantum gates and quantum simulator. The wide library of electron and nuclear spin combinations is particularly attracting for quantum error correction. In addition, they can retain most of their magnetic features once they are put in contact with conducting substrates, a necessary step for integration in devices.

Our research has been focused on the rationalization of the main parameters governing spin dynamics in magnetic molecules, with a special attention for vibrational properties, indeed the Achille's heel of magnetic molecules.³ Our efforts have been directed also to molecules that can be deposited on a surface and addressed using scanning probe techniques, such as metal phthalocyanines⁴ and organometallic sandwich compounds.⁵



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- [1] M. Atzori and R. Sessoli, *J. Am. Chem. Soc.*, 2019, **141**, 11339.
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 - [4] L. Malavolti et al., *Nano Lett.*, 2018, **18**, 7955.
 - [5] L. C. de Camargo et al. *Angew. Chem. Int. Ed.*, 2021, **60**, 2588.

Microwave Cavities for Materials Characterisation

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We have used resonant microwave techniques in many interdisciplinary studies involving the non-invasive characterisation of materials and material processes [1]. This has involved new innovations in EPR, such as the development of the dual mode EPR reactor resonator [2]. Prior to this we have investigated the separate response of materials to microwave electric and magnetic fields, owing to the spatial separation of the EM waves that occurs naturally as a result of the standing wave pattern set up within resonant cavities. The same cavities double up as sensors (at low field amplitudes) and actuators (at high field amplitudes), opening up the opportunity for simultaneous measurement of material properties whilst heating is occurring by switching between these two modes of operation.

This presentation will review a variety of material studies that use novel, bespoke microwave cavities, from the simultaneous electrical/structural characterisation of ammonia absorption in solids using a combination of microwave absorption and neutron diffraction, to their use in selective laser melting for additive manufacturing. It concludes with a summary of recent developments in X-band EPR cavity design and related topics, such as electronic tuning of the coupling structures and miniaturised cavities, offering very high sample filling factor whilst maintaining high Q.

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[2] A. Folli, H. Choi, M. Barter, J. Harari, E. Richards, D. Slocombe, A. Porch, D. M. Murphy, *J. Magn. Reson.* 2020, **310**, 106644. DOI: 10.1016/j.jmr.2019.106644.

Exploring photogenerated molecular quartet states as spin qubits

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Photogenerated molecular spin systems hold great promise for applications in quantum information science (QIS) because they can be prepared in well-defined spin states and their properties can be tuned, virtually at will, by chemical synthesis [1].

Importantly, compared to mesoscopic solid-state materials, like NV⁻ centres, molecular systems are scalable and offer structural reproducibility and modularity with atomic precision [2].

One of the current major challenges in QIS is the identification of suitable molecular qubit candidates. In this contribution, we are addressing this challenge by exploring the possibility of using photogenerated molecular quartet states as multi-level spin qubits using femtosecond UV-vis absorption and transient EPR spectroscopies.

The investigated model system is composed of a PDI chromophore strongly coupled to a covalently-linked stable radical. After photoexcitation, a spin polarised molecular quartet state is formed as confirmed by transient nutation experiments. By analysis of its magnetic properties using pulse EPR, we show that this quartet state has characteristics required for quantum logic and memory applications and is thus viable as a spin-based molecular qubit: It can be initialised by light in a highly pure initial state, is long-lived, and exhibits coherence times that are much longer than typical pulse microwave-driven gate operation times, even at modest temperatures [3].

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Spin Polarized Triplet States and Radical Pair States in Heliobacterial Reaction Centres

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Heliobacteria are soil-dwelling strictly anaerobic photosynthetic bacteria that live in a symbiotic relationship with plants and play an important role in nitrogen fixation. To deal with the low intensity infrared light present in the soil environment they use bacterial chlorophyll *g* (BChl *g*) as the main chromophore in their reaction centre (HbRC) protein complexes and are the only known organism to do so. The HbRC is a homodimeric protein with exact C₂ symmetry. If HbRC are exposed to oxygen the BChl *g* isomerizes to chlorophyll *a_F* (Chl *a_F*) and the photosynthetic apparatus becomes non-functional. This naturally occurring process, provides a unique opportunity to study the effect of subtle changes in the chlorophyll on the energy and electron transfer in the RC with out resorting to mutations or other methods that alter the structure of the complex. We have used transient EPR, pulsed ENDOR and ODMR spectroscopy to study the changes in the HbRC as the BChl *g* is converted to Chl *a_F*. The transient EPR data show that electron transfer kinetics are altered and suggest that this occurs when one of the chlorophylls of the primary donor, P₈₀₀⁺ is converted creating a heterodimer. This is borne out by the ENDOR studies and DFT calculations that show greater localization of the unpaired electron of the donor radical cation in the heterodimer. Triplet states are also observed in the antenna chlorophylls of the complex. The ODMR measurements reveal that there are two pools of in BChl *g* molecules in different local environments that form triplet states with different zero-field splitting parameters. Moreover, these two pools have different sensitivities to oxygen. Using the recently published x-ray structure and estimates of the excitonic coupling between the antenna chlorophylls we are able to propose possible sites for the triplet states.

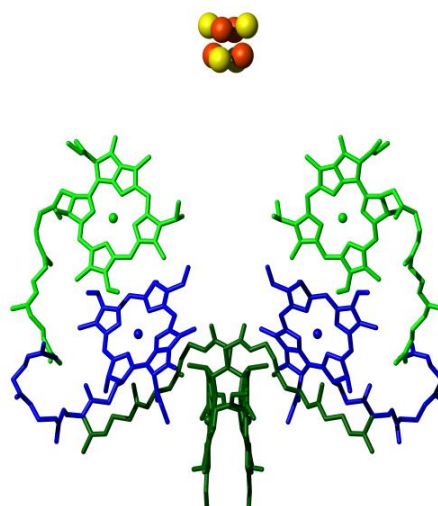


Figure 1. Structure of the electron-transfer cofactors of HbRC's¹. The pair of dark green BChl *g* molecules at the bottom are the primary donor P₈₀₀

[1] Gisriel, C., Sarrou, I., Ferlez, B., Golbeck, J. H., Redding, K. E., and Fromme, R. (2017), Science 357(6355), 1021-1025.

Controlling Electron-Nuclear Spin Couplings in Molecular Magnets

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This talk will highlight recent efforts at the US National High Magnetic Field Laboratory (MagLab) focusing on electron-nuclear spin interactions in magnetic molecules using broadband pulsed EPR methods. This work is of both fundamental and practical interest in areas of research ranging from coordination chemistry to quantum information science. After a short introduction to recent technique developments at the MagLab, the talk will focus on efforts aimed at controlling electron-nuclear couplings in various lanthanide containing magnetic molecules that could potentially be of utility in future quantum technologies. In particular, I will show how weak super-hyperfine interactions can be detrimental to quantum coherence and describe strategies for mitigating such influences, whereas very strong hyperfine coupling may actually be beneficial. The first example involves recent experimental and computational work exploring the decoupling of electron and nuclear spins at so-called atomic-clock transitions (ACTs), as monitored via electron-spin-echo envelope modulation (ESEEM) measurements [1]. ACTs occur at avoided level crossings associated with the Zeeman splitting of a pair of magnetic sub-states, resulting in an operating region over which the electron spin resonance (clock) transition frequency becomes insensitive to the local magnetic field ($g_{\text{eff}} = 0$) and, hence, immune to magnetic noise [2]. It is this property that gives rise to the exceptional phase stability of atomic clocks and can also significantly enhance the coherence of spin qubits. For integer spins, avoided crossings may be generated and controlled via the crystal-field interaction while, for half-integer spins, the electron-nuclear hyperfine interaction serves the same role. Indeed, the second example that will be presented is that of ACTs associated with lanthanide ions possessing synthetically controllable hyperfine interactions that are exceptionally strong.

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Using pulsed-EPR in the analysis of integral membrane proteins

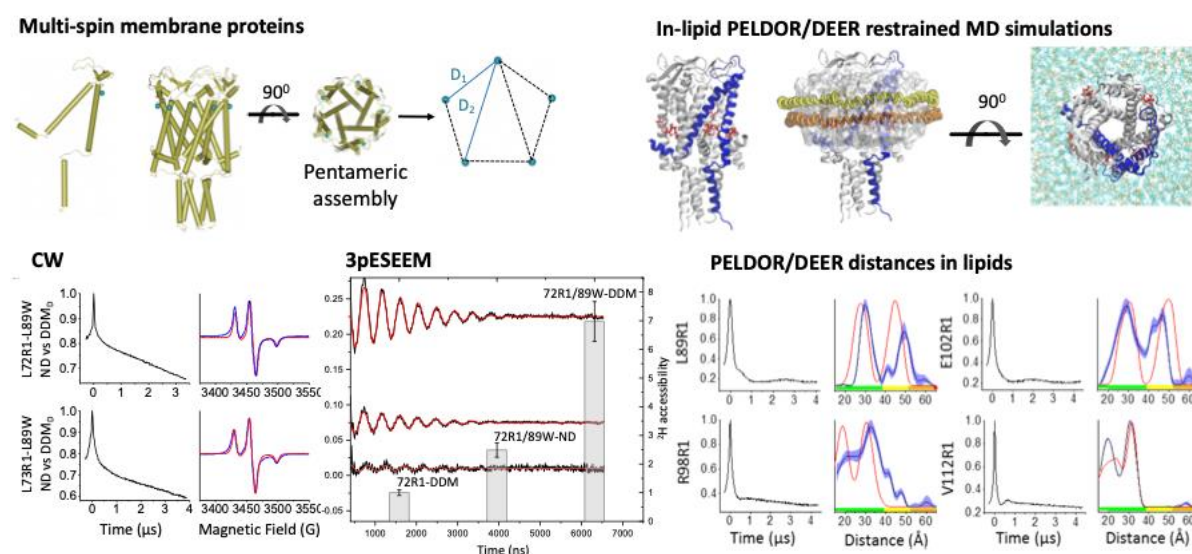
Christos Pliotas^{1,2}, Charalampos Kapsalis², Yue Ma¹, Bolin Wang¹, Benjamin J Lane¹, Andrew M Hartley¹, Hassane EL Mkami³, Bela E Bode²

¹Astbury Centre for Structural Molecular Biology, University of Leeds, UK

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PELDOR (or DEER) and ESEEM have emerged as powerful tools for assessing membrane protein conformation, folding, oligomerisation and dynamics. PELDOR can provide accurate quantification of the conformational equilibria of membrane proteins, dovetailing well with techniques such as X-ray crystallography and cryo-EM. 3pESEEM spectroscopy can offer deuterium accessibility quantification at a single residue level. Additionally, computational tools can be tailored to incorporate experimentally derived PELDOR distance restraints to reveal the complete conformational ensemble of membrane proteins. Here, we will focus on our recent work on the mechanosensitive channel MscL and highlight the EPR tools we used to elucidate its gating mechanism. Further, we will discuss recent developments in the availability of lipid scaffolds that limit the impact of protein solubilisation and offer flexibility of choice in lipid composition, a key factor in the functional integrity of membrane proteins.



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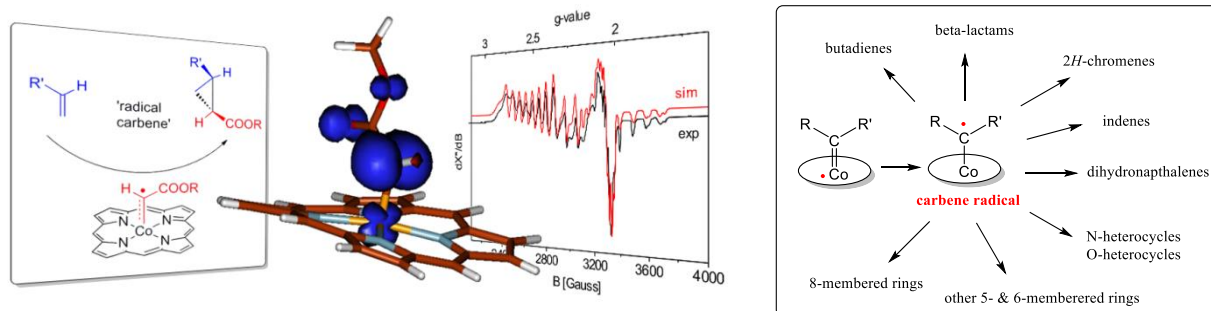
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Catalytic Metalloradical Reactivity of Carbenes & Nitrenes

Bas de Bruin

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Radicals are intrinsically reactive, but in the coordination sphere of transition metals highly selective radical-type processes are certainly possible. Inspired by the intriguing catalytic radical-type transformations mediated by metalloenzymes, we are actively investigating new catalytic transformations mediated by synthetic (open-shell) organometallic catalysts. Special interest in such open-shell organometallic species comes from their different reactivity compared to their closed-shell counterparts.[1] In particular, metalloradical complexes allow us to steer and control a variety of unprecedented radical-type reactions.



In this contribution the metalloradical reactivity of cobalt(II) catalysts with nitrene and carbene precursors will be discussed. Formation of nitrene & carbene radicals in the coordination sphere of cobalt plays a key role in these reactions.[1-6] Reactivity studies, EPR spectroscopy and complementary DFT calculations are used to unravel the open-shell pathways of the paramagnetic metalloradical intermediates. This presentation will primarily focus on EPR characterisation of the key intermediates.

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- [5] a) te Grotenhuis, C.; Das, B.G.; de Bruin, B. *et al.*, *Chemical Science* **2017**, 8, 8221. b) te Grotenhuis, C.; de Bruin, B. *et al.*, *Angew. Chem. Int. Ed.* **2018**, 57, 140. c) M. Zhou, B. de Bruin, *et al.*, *Angew. Chem. Int. Ed.* **2020**, 59, 11073–11079.
- [6] a) N.P. van Leest, B. de Bruin, *et al.*, *ACS Catalysis* **2020**, 10, 7449–7463. b) N.P. van Leest, B. de Bruin, *et al.*, *J. Am. Chem. Soc.* **2020**, 142, 552–563.

Role of magnetic anisotropy in paramagnetic relaxation enhancement

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Nuclear magnetic resonance (NMR) of paramagnetic metal complexes remains a challenging but highly informative analytical technique. The major difficulty is coming from the paramagnetic relaxation enhancement (PRE) that broadens NMR lines beyond detection for nuclei in the vicinity of the paramagnetic centre. However, in some paramagnetic metal complexes the relaxation enhancement is not as dramatic, as shown by a recent example of measured ¹H NMR signal of a proton directly attached to an intermediate spin iron(II) at –3560 ppm at 295 K.[1]

We have previously demonstrated that magnetic anisotropy alters both Curie and dipolar relaxation mechanisms in lanthanide complexes especially at low magnetic field.[2] In this work we analyse how magnetic anisotropy alters magnetic field dependence of the PRE. Using *ab initio* theory, Nuclear Magnetic Resonance (NMR) and advanced Electron Paramagnetic Resonance (THz-EPR), we analyse in details PRE and shift data in *t*Bu(PNP)Fe–H complex and show how zero-field splitting can slow down dipolar relaxation (Figure 1).

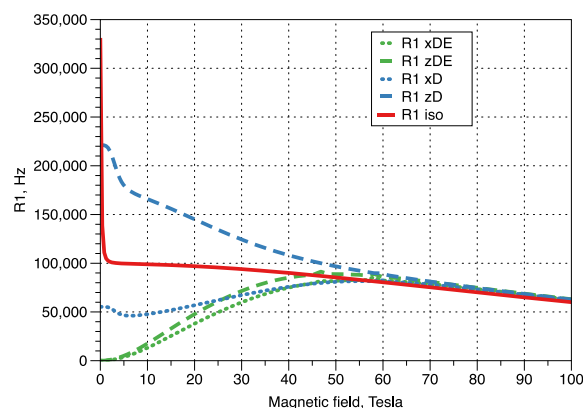


Figure 1. Simulated dipolar longitudinal relaxation rates (R_1) as a function of the magnetic field. The model for a point paramagnetic center with $S = 1$ and ^1H located 1.57 Å away either along x-axis (dotted lines) or z-axis (dashed lines). The relaxation profile when no ZFS is present is shown in red, the case of axial ZFS with $D = -56 \text{ cm}^{-1}$ is shown in blue and rhombic ZFS with $E = -13.8 \text{ cm}^{-1}$ is shown in green.

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EPR into the Almost Optical Region: Applications to Coordination Complexes

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Electron paramagnetic resonance (EPR) spectroscopy has been successfully applied to coordination complexes of transition metal (d block) ions for many years. The bulk of such studies employs X-band microwave radiation (~ 9.3 GHz, 0.31 cm⁻¹), with Q-band (35 GHz, 1.17 cm⁻¹) EPR also being very fruitful, as shown by Hoffman, particularly for metalloenzymes.¹ The resonant magnetic fields rarely exceed 1.5 T. A limitation of these techniques thus occurs when paramagnets with $S \geq 1$ experience zero-field splitting (ZFS) that is much larger than the above energies. In such cases, EPR spectra either cannot be recorded, or are relatively uninformative. A solution is to extend the frequency, and correspondingly the resonant field range, ever higher. High-frequency and -field EPR (HFEPR), at NHMFL, routinely goes to 600 GHz with fields up to 15 T and provides informative spectra for complexes of ions such as Mn^{III} ($3d^4$, $S = 2$),² which generally has an orbitally isolated ground state. In many cases, such as when there is orbital (near) degeneracy, the ZFS is still too large for full analysis by HFEPR and frequencies into the far-infrared (FIR) region (~ 100 cm⁻¹ and higher) are needed. This can be achieved using either a standard FIR source³ or coherent synchrotron radiation in the THz region.⁴ In each spectrometer setup, the source is combined with an external magnet that can be set to fields in the range $0 - 10$ T, allowing discrimination between magnetic and vibrational (phonon) transitions. Applications to lower-coordination number (tri- and tetra-coordinate) complexes of Fe^{II} ($3d^6$, $S = 2$) and Co^{II} ($3d^7$, $S = 3/2$) will be described.

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Dressing up electron spins to (un)lock their potential: Application to distance measurements between trityl radicals

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The longest electron-electron distance that can be measured with pulsed dipolar spectroscopy (PDS) is determined by the phase memory time T_m of the electron spins. This is the case for all available methods (DEER, SIFTER, DQC, RIDME).

We recently recognized that the rotating frame relaxation time $T_{1\rho}$ of trityl radicals is orders of magnitude longer than T_m , see Figure 1. This is nice, but useless on its own with respect to PDS. To make use of this feature, one has to be able to measure the dipolar coupling *during* the spin lock.

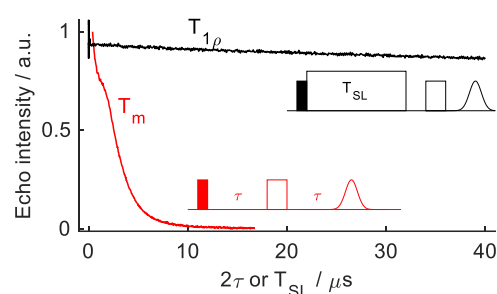


Figure 2. Phase memory and longitudinal rotating frame relaxation time of a bis-trityl ruler. The gate length of our TWT is 50 μ s.

Luckily, this is indeed possible. Using a bis-trityl ruler of 4.1 nm length, we found a way to observe dipolar modulations by applying short periods of phase modulation, generated by an AWG, during the spin lock. The frequency of these phase modulations matches the nutation or Rabi frequency of the locking pulse. Because these phase-pulses act on the combined states of spins and microwave irradiation, this is termed *dressed* ESR.[1,2] Similar approaches exist in MRI,[3] NMR,[4] and quantum information processing.[5]

In this contribution, I will explain the principle behind dressed ESR with phase-modulated pulses and why it is possible to measure the dipolar coupling with it. After this, I will discuss technical and conceptual problems and possible further steps.

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Sub-nanotesla Magnetometry with a Fibre-Coupled Diamond Sensor

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The negatively charged nitrogen-vacancy (NV) centre in diamond is a colour centre that is one of the most-studied defects in the solid-state. Optically-detected magnetic resonance of the NV centre [1] allows it to be used as a magnetometer [2]. Diamond-based magnetometers have already found use in a range of applications for example in the detection of single-neuron action potentials [3]. However, many of these set-ups are confined to optical tables and thus their portability and applications are limited. Here a fibre-coupled sensor that reaches the sensitivity of 310 ± 20 pT/Hz^{1/2} in the frequency range of 10-150 Hz is presented [4]. We have also demonstrated it is possible to locate damage in steel using a similar configuration [5]. The targeted application for this magnetometer is in the detection of cardiac magnetic fields for magnetocardiography (MCG). Heart-related illnesses are among the leading causes of death globally and hospitals currently use electrocardiography (ECG) to detect cardiac issues. MCG has been demonstrated to be diagnostically superior to ECG [6]. However, current MCG uses magnetometers, such as the superconducting quantum interference device (SQUID), which are too expensive to allow widespread use [7]. A sensor such as ours based on NV centres may be more practical for medical applications if the sensitivity can be improved.

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Highly Resolved Hyperfine Lines in Organic Radicals using Rapid-Scan Electron Paramagnetic Resonance

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Rapid Scan EPR (RS-EPR) has been shown to improve signal-to-noise ratios in spectra of a variety of radicals [1], especially those with long relaxation times [2], and has been beneficial in spin-trapping experiments [3] and EPR imaging [4]. The resolution of RS-EPR spectra for samples with many narrowly-spaced hyperfine lines is examined in this study. X-band (ca. 9 GHz) fluid solution RS-EPR spectra were acquired for 3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy (CTPO), diphenylnitroxide (DPNO), galvinoxyl, and perylene cation radical. These data demonstrate the capabilities of the rapid-scan technique to characterize very well-resolved hyperfine couplings and linewidths as small as 30 mG [5]. Relevant experimental parameters are discussed, and a comparison with continuous wave EPR (CW-EPR) is made. In RS-EPR the signal bandwidth should be less than resonator bandwidth to achieve minimum linewidths. Signal bandwidth is inversely proportional to linewidth and proportional to RS scan rate, while resonator bandwidth is inversely proportional to resonator Q. Proper selection of scan rate and resonator Q is needed to achieve resolution of closely-spaced narrow EPR lines. Example calculations are given. Spectra are shown that were obtained on two spectrometers - a locally-modified Bruker E500T in Denver and a Bruker Elexsys spectrometer with Bruker rapid-scan accessory.

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Electron Spin Decoherence In Deuterated Environments

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Understanding the decoherence behavior of electron spins in matrices containing nuclear spins is relevant to pulse dipolar EPR spectroscopy and potential applications of spin qubits. For many environments, the electron spin decoherence behavior (measured via Hahn echo decay) can be quantitatively predicted using the Hilbert-space many-body spin dynamics technique, Cluster Correlation Expansion (CCE) [1,2]. CCE has been used to predict electron spin decoherence in ^1H -rich environments, crystals [3] and frozen solvents [4]. However, pulse dipolar EPR experiments on spin-labeled proteins are often performed in deuterated solvents with protiated proteins — a partially deuterated spin-dense matrix. The application of CCE here is not so straightforward as the longer timescales, correlation effects, and the spin-1 nature of deuterium introduce new challenges. This work aims to overcome these obstacles and produce quantitative coherence predictions. The predictions are compared to experimental data obtained for nitroxides in partially deuterated solvents.

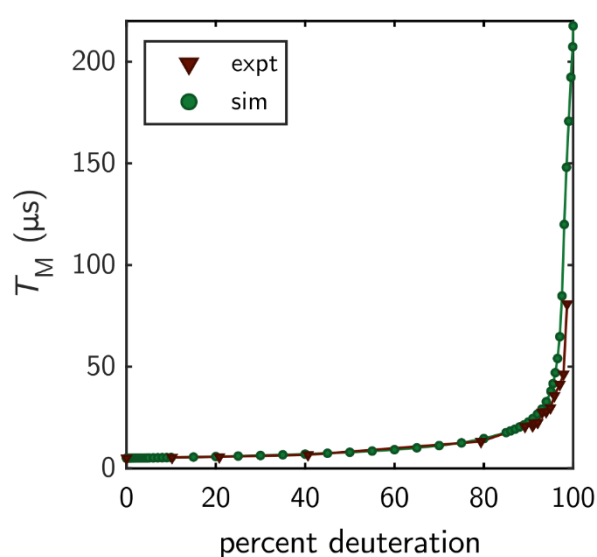


Figure: The decoherence time for d_{18} -TEMPO in water:glycerol is shown vs. percent matrix deuteration. The experimental data are indicated with triangles and the simulated data are marked with circles. The basic shape of the curve can be understood by noting that the coherence time scales as $1/[\text{}^1\text{H}]$ at high $[\text{}^1\text{H}]$ and as $1/[\text{}^2\text{H}]$ at low $[\text{}^1\text{H}]$, with some cross-over region [5].

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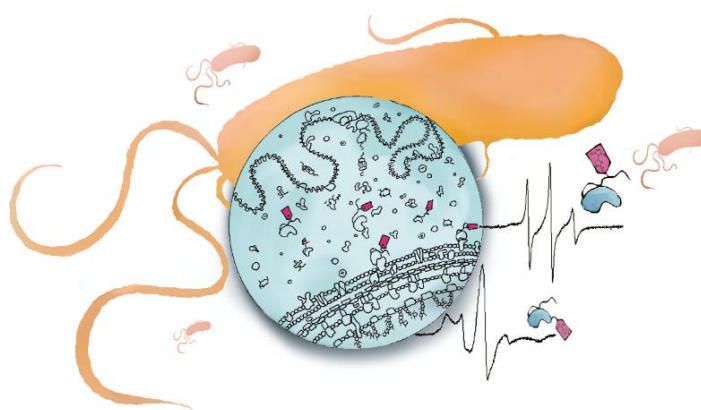
Nitroxide-based SDSL-EPR for the study of protein dynamics in living cells

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In the last two decades, the structural biology community has shown great interest in the study of proteins in their native environment. Because of this, remarkable progress in the development of new “*in-cell*” approaches have been made. Among them, Site-Directed Spin Labeling (SDSL) coupled to Electron Paramagnetic Resonance (EPR) Spectroscopy exhibits competitive and advantageous features to capture protein dynamics inside cells [1–3]. In particular, nitroxide-based SDSL-EPR couples the benefits of high sensitivity and the lack of size constraints for the biomolecule of interest with the ability to study protein structural transitions and interactions at physiological temperature.

In this work, using our efficient delivery protocol we achieved to study the structural dynamics of a flexible chaperone protein, NarJ, directly inside its endogenous host, the *Escherichia coli* bacterium. The NarJ chaperone is involved in metal cofactor acquisition by the nitrate reductase respiratory complex [4-5]. By using cw-EPR and pulsed dipolar spectroscopy (DEER experiments) we revealed the site-specific structural behaviour of NarJ directly in *E. coli* and compared those data with the ones obtained *in vitro*. Finally, we were able to prove that the delivered NarJ was active inside cells, being able to restore nitrate reductase activity in a strain deleted of the *narJ* gene. This work represents a new step in the development of biostructural *in-cell* EPR and opens new perspectives to address structural biological questions directly inside the cell.



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Functional basis of electron transport within photosynthetic complex I

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In respiration and photosynthesis large bioenergetic machines use electron-transfer centres to build up the electrochemical gradient required for ATP synthesis. EPR has long been a powerful technique used to understand the role of such centres. However, these membrane proteins are often tightly regulated, labile and limiting to cell growth, hindering our ability to isolate and characterise them. Photosynthetic complex I (PS-CI) is a prominent example and consequently its mechanism is not understood.

Exploiting recent EPR sensitivity advancements [1], we are able to characterise the three overlapping [4Fe-4S] cluster EPR signals from PS-CI in two cyanobacterial strains at low concentration (<10 μ M) using relaxation-filtered pulse EPR, and to determine their structural position with orientation selective DEER. Using small volume potentiometric EPR titrations we establish the redox potentials of the Fe-S clusters, placing PS-CI for the first time into the biogenetic map of photosynthesis [2].

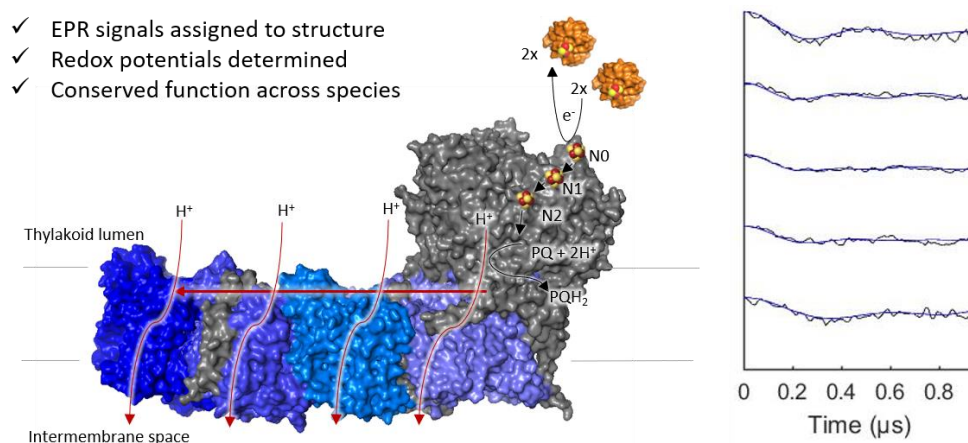


Figure: Structure and proposed catalysis of *T. elongatus* PS-CI (PDB: 6HUM)[3]. Proton pumping subunits (blues) and putative proton movement indicated by red arrows. Electron transfer from ferredoxin (orange) to plastoquinone is indicated by black arrows. Right: Orientation selective DEER spectra (black) and simulated best-fits (blue) for the cluster positions shown on the structure.

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In situ EPR identification of active sites in FeNC catalysts for the oxygen reduction reaction and mechanism underlying Cr/PNP based ethylene tetramerisation catalysis

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Energy storage, clean energy conversion and the development of sustainable chemistry involving earth abundant transition metals (TM) are highly relevant topics of current research. Despite tremendous advances in catalysis research, the quest for alternatives to precious metal catalysts with high stability and activity persists. Knowledge based development of efficient TM catalysis requires exact information about the identity, oxidation state and structure of active catalytic sites. TM catalysis frequently involves paramagnetic states accessible to EPR. In this regard, we use in situ EPR for mechanistic understanding of the FeNC catalysts used for the oxygen reduction reaction (ORR) and Cr/PNP based ethylene tetramerisation catalysis.

Fuel cells are promising candidates for the usage of H₂ from sustainable sources. To replace platinum catalysts for the ORR in fuel cells, iron macrocycles integrated in carbon matrices, referred to as FeNC catalysts, are regarded favourable substitutes. However, the structure of their active iron site remains unclear. EPR in combination with in situ ⁵⁷Fe Mössbauer spectroscopy and DFT has recently provided new insight into the coordination of FeN₄ moieties in different FeNC catalysts.¹ This work has been extended to EPR under applied potential to monitor the iron sites during catalytic activity. Herein, first results obtained on FeNC catalysts will be presented.

Experimental evidence for a bis-ethylene chromium(I) motif the postulated but previously unobserved key intermediate, in the metallacyclic mechanism for ethylene oligomerisation is obtained for the first time.² This transformation provides a selective industrial route to linear α -olefins such as 1-hexene and 1-octene, which act as co-monomers for the production of polyethylene. Isotope labelling and EPR studies of Cr/PNP based catalytic systems not only helped in the identification of coordination sphere of this key intermediate but also opened a new route towards mechanistic studies of selective ethylene tetramerisation. Herein, we present new insights into the mechanism of its formation derived from quantum chemistry.

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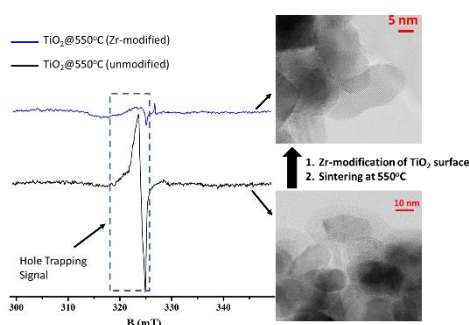
EPR Investigation of the Effect of Chemical Modification on the Charge Carrier Trapping in TiO₂ Nanoparticles

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Trapping of charge carriers at surfaces and interfaces in thin films of nano porous metal oxide (such as TiO₂) is generally considered as one of the major limiting factors for achieving the maximum theoretical efficiency of devices such as Solar Cells.¹ The present work aims to identify factors responsible for such charge carrier trapping by a combination of theoretical modelling and spectroscopic, microscopic, electronic as well as electrochemical characterization, to design suitable modifications for the improvement of charge carrier mobility within these nano porous metal oxide films. TiO₂ single crystalline nanoparticles (anatase) of defined shape and size have been used as a model system for this study. X-band electron paramagnetic resonance (EPR) spectroscopy has been utilized to understand and quantify the local defect structure² in these TiO₂ nanoparticles before and after high temperature sintering. Control EPR experiments with suitable electron and hole quencher have been employed to distinguish between EPR signals related to surface and interfacial/grain boundary region. Chemical modification of the surface of TiO₂ nanoparticles with zirconium (Zr) followed by high temperature sintering has been found to selectively quench some of the photogenerated EPR signals associated with grain boundary traps. Moreover, EPR study with commercial anatase TiO₂ also leads to the same conclusion. This observation supports the theoretical prediction that partial substitution of surface Ti⁴⁺ with Zr⁴⁺ prevents the formation of intra band gap states in anatase TiO₂.³



Scheme 1: EPR spectra of unmodified and Zr-modified TiO₂ in presence of continuous UV radiation at 77 K under vacuum showing the effect of Zr-modification on the hole trapping signal of anatase TiO₂.

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EPR characterisation of a doped organic semiconductor

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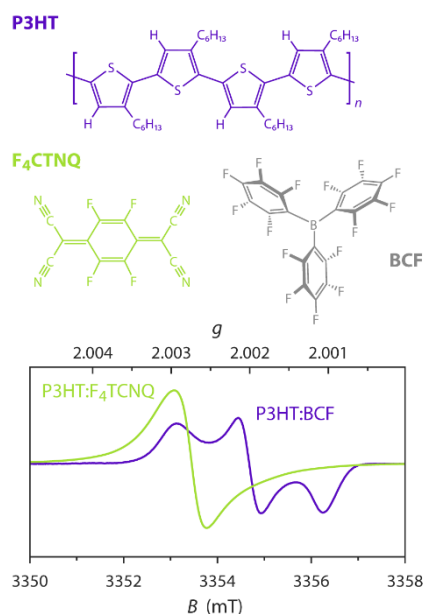
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Controlled, efficient and stable doping of organic semiconductors for the enhancement of electrical conductivity is a crucial requirement for their widespread use in opto-electronic applications. Successful doping requires an electron transfer between host and dopant molecules as well as separation of the resulting ion pair to generate free mobile charge carriers in the host matrix.¹ Electron Paramagnetic Resonance (EPR) spectroscopy is an ideal tool for the identification of the paramagnetic species introduced by doping and characterisation of their interactions with the molecular environment.^{2,3}

In a multi-frequency continuous wave and pulse EPR study, we investigated p-type doping of the prototypical electron donor polymer poly(3-hexyl-thiophene) (P3HT) with two different dopants: 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) and tris(pentafluorophenyl)borane (B(C₆F₅)₃, or BCF). The EPR results revealed the P3HT radical cation as the only paramagnetic species in BCF-doped films, while the EPR spectra for F₄TCNQ-doped P3HT in solutions and films are determined by the presence of both the P3HT radical cation and the F₄TCNQ radical anion. Pulse EPR measurements, including hyperfine techniques and nutation experiments, helped unravel different spectral contributions that suggest the presence of a range of different environments for the P3HT radical cation in F₄TCNQ-doped films.



Molecular structures of the organic semiconductor and dopants and W-band cw EPR spectra recorded on powders of BCF- and F₄TCNQ-doped P3HT films.

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EPR verified metallocenate derivatives of Mn(I), Fe(I), Co(I)

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The chemical characterisation of ferrocene over 65 years ago was revolutionary in shaping contemporary organometallic chemistry.[1] While ferrocenium cations were discovered soon after, it took until 2016 for a ferrocenium dication to be isolated.[2] The mono-anion of ferrocene has only been detected by low temperature electrochemical studies to date.[3] Here we report the isolation of a derivatized ferrocene anion in the solid state as part of an isostructural family of temperature sensitive 3d metallocenates (including Mn(I) and Co(I) analogues).[4] Rapid decomposition above -30 °C hinders characterisation with NMR spectroscopy and SQUID magnetometry. These systems are verified via single-crystal XRD, cyclic voltammetry, ATR-IR and Raman spectroscopies, and elemental analysis. X- and Q-band continuous wave EPR measurements for each analogue are in agreement with *ab initio* calculations, and the Fe analogue is further characterised using ⁵⁷Fe Mössbauer spectroscopy. These data have allowed us to map the electronic structures of this metallocenate family, providing textbook examples of such materials and opening up new chemical space for future exploration.

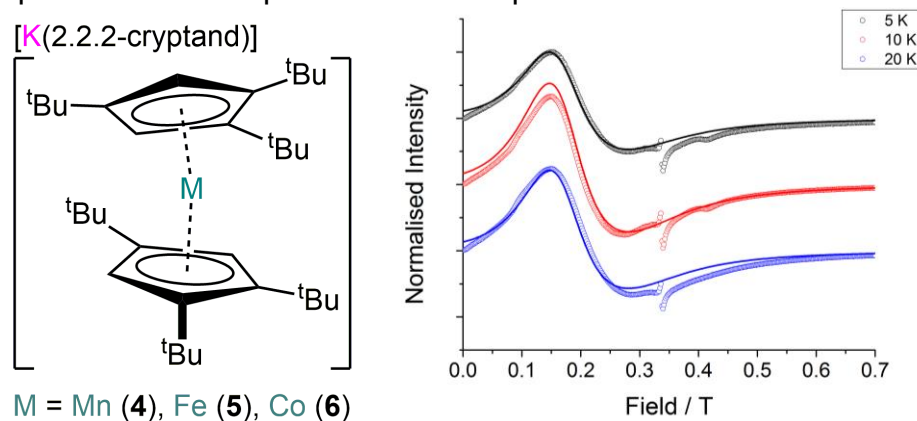


Figure 1. Left) Formula of the metallocenate anion which crystallises with the K(2,2,2-cryptand) cation and right) CW X-band EPR spectrum of Fe(I) collected at 5, 10 and 20 K

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Toward Visible Light-Activated Molecular Grippers

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The molecular machines triggered and controlled by light are attractive targets for applications in nanoelectronics. A next generation of resorcin[4]arene cavitands, equipped with diverse quinone (**Q**) and [Ru(bpy)₂dppz]²⁺ (bpy=2,2'-bipyridine, dppz=dipyrido[3,2-a:2',3'-c]phenazine) photosensitizing walls in different configurations, were synthesized and investigated.[1] Upon visible-light irradiation at 420 nm, electron transfer from the [Ru(bpy)₂dppz]²⁺ to the **Q** generates the semiquinone (**SQ**) radical anion, triggering a large conformational switching from a flat *kite* to a vase geometry with a cavity for the encapsulation of small molecular guests. Depending on the molecular design, the **SQ** radical anion can live for several minutes (≈10 min) and the vase can be generated in a secondary process without a need for addition of a sacrificial electron donor to accumulate the **SQ** state. Switching can also be triggered by other stimuli, such as changes in solvent, host–guest complexation, and chemical and electrochemical processes, as monitored by NMR, UV-Vis and cw-EPR spectroscopies as well as EPR/UV-Vis spectroelectrochemistry. This comprehensive investigation benefits the development of stimuli-responsive nanodevices, such as light-activated molecular grippers.



Fig. 1 Resorcin[4]arene cavitands can be switched between a *kite* conformation, adopted in the dark, and a vase, generated under visible light. The switching is triggered by the formation of a **SQ** radical anion through a photosensitizing process. The cavitands resembles the mechanical switching occurring in some flowers that bloom open in the evening and close during the day (figure design: Ella Maru Studio).

[1] V. Garcia-Lopez, M. Zalibera, N. Trapp, M. Kuss-Petermann, O. S. Wenger, F. Diederich, *Chem. Eu. J.* 2020, **26**, 11451–11461.

Ensemble modelling of intrinsically disordered protein domains with EPR-derived distance distributions: The case of hnRNP A1

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Distance distributions in the nanometre range, as provided by pulsed dipolar EPR spectroscopy, are a unique source of information on the width of the conformational ensemble of disordered protein domains. It is advantageous to complement them by structural information obtained at ambient temperature in integrative structural biology approaches. However, before such integration we would like to know whether ensemble modelling with only distance distribution restraints (DDRs) is robust. Here, we address this question for the case of the low-complexity domain of heterogeneous nuclear ribonucleoprotein A1 (hnRNP A1), a human protein predominantly active in mRNA regulation. For characterizing structure of this 133-residue intrinsically disordered domain, we have obtained 16 DDRs between sites in the structured domain and 3 DDRs between sites that are both in the low-complexity domain. We discuss how modelling of the ensemble [1,2] is affected by the approach used for converting primary DEER data to distance distributions and how one can establish that the restraint set is sufficient and consistent.

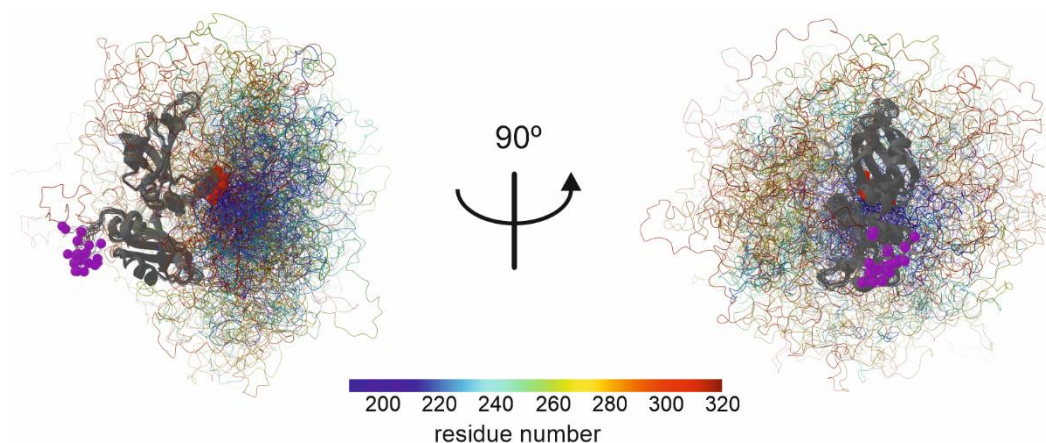


Figure Cartoon representation of the ensemble model of hnRNP A1. The RNA recognition motifs are shown in grey, their N termini by purple sphere, and their C termini by red spheres. The low-complexity domain (residues 188-320) is represented by a coil model with colour gradient along the chain.

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High sensitivity Gd^{3+} - Gd^{3+} EPR distance measurements that eliminate artefacts seen at short distances

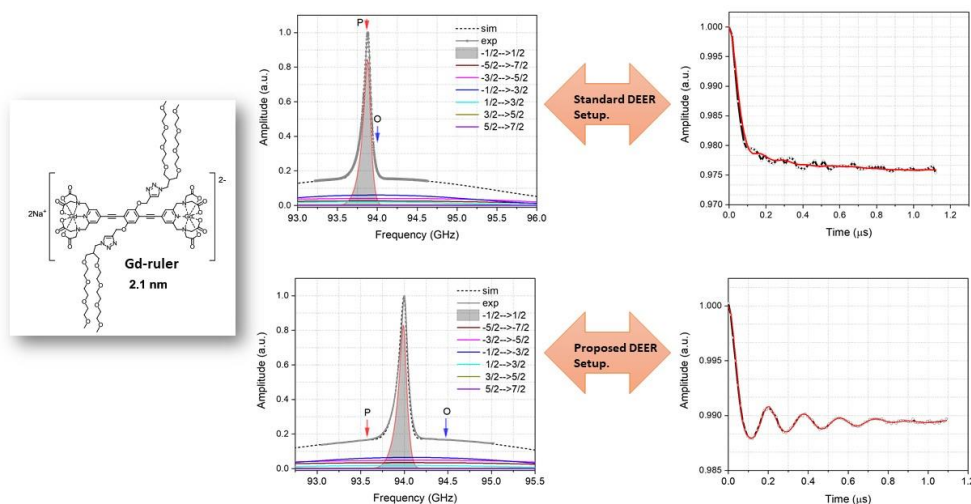
Hassane EL Mkami¹, Robert I. Hunter¹, Paul A. S. Cruickshank¹, Michael J. Taylor¹, Janet E. Lovett¹, Akiva Feintuch², Mian Qi³, Adelheid Godt³, Graham M. Smith¹.

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Gadolinium complexes are attracting increasing attention as spin labels for EPR dipolar distance measurements in biomolecules and particularly for in-cell measurements. However, it has been shown that unwanted flip-flop transitions within the central transition of the high spin Gd^{3+} ion can introduce artefacts in dipolar distance measurements, particularly when measuring distances less than 3 nm. Previous work has shown some reduction of these artefacts through increasing the frequency separation between the two frequencies required for the Double Electron-Resonance (DEER) experiment. Here, by using a wideband induction mode sample holder at 94 GHz, we show through series of DEER measurements on two Gd rulers, with Gd–Gd distances of 2.1 and 6.0 nm, that such artefacts can be eliminated by avoiding excitation of the central transition by both the pump and observer pulses. We demonstrate that in such setup an excellent signal-to-noise ratio is still maintained.



H.EL Mkami et al, Magn. Reson., 1, 301–313, 2020; <https://doi.org/10.5194/mr-1-301-2020>

The Structure of Lipid Rafts in Model Biological Membranes by DEER of Spin-Labeled Cholesterol Analog

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The plasma membranes are assumed to be highly compartmentalized which could be an important prerequisite for the membrane protein functionality. The liquid ordered–disordered phase segregation of lipids in the membranes results in formation of nanoscale liquid-ordered assemblies – lipid rafts, – which are enriched with cholesterol and saturated chain lipids. Lipid rafts are assumed to be involved in a variety of cell functions such as sorting, signaling, endocytosis, and protein activity. The structure of rafts, their dynamics, physiological importance, and other properties have not still been clearly understood. Problems appearing in their investigation are related mainly with their small (nanoscale) size and with their transient nature.

Double electron-electron resonance spectroscopy (DEER, also known as PELDOR) is sensitive to spin-spin dipolar interactions between spin labels just at the nanoscale range of the inter-spin distances. In this work, we apply DEER to study spin-labeled cholesterol analog - 3 β -doxyl-5 α -cholestane diluted in bilayers comprised of equimolar mixture of saturated dipalmitoyl-glycero-phosphocholine (DPPC) and unsaturated dioleoyl-glycero-phosphocholine (DOPC) phospholipids. This mixture, with cholesterol also added, is known for its ability for raft formation. The data obtained clearly indicate that DEER approach indeed is sensitive to the presence of lipid rafts in the membranes. A new information was obtained on the raft structures: the peculiarities of cholesterol mutual lateral disposition, the cholesterol concentration in the rafts, and others.

DEER and RIDME Measurements of the Nitroxide-Spin Labelled Copper-Bound Amine Oxidase Homodimer from *Arthrobacter Globiformis*

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Pulse dipolar spectroscopy (PDS) can be an invaluable tool in the study of biological systems as the methods can help to elucidate nanometre-scale distances through measurement of dipole-dipole interactions between paramagnetic centres. In this work, Double Electron Electron Resonance (DEER) and Relaxation Induced Dipolar Modulation Enhancement (RIDME) experiments are performed on the copper amine oxidase from *Arthrobacter globiformis* (AGAO) (Fig. 1), where multiple nanometre-scale distances are available for measurement between nitroxide spin labels and bound Cu(II) paramagnetic centres. Protein modelling methods are also employed to aid identification of distance measurements within the AGAO homodimer. By comparison of results retrieved through experimental and modelling methods, we find that the measured distances are consistent with the surface Cu(II) binding sites being occupied, while the active sites are not. We show that, through selection of optimal experimental parameters and careful data analysis, two distinct distances can be measured, with the longer of the two exceeding 5 nm. We also discuss that, as a result of this parameter optimisation, RIDME experiments may be preferable to DEER for measurement of these long distances. [1]

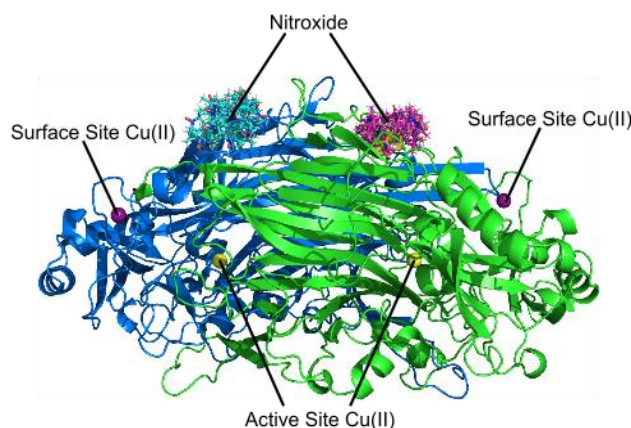


Fig. 1 Model of AGAO derived using MD simulations. MMM rotamer spin-labels and bound Cu(II) ions are labelled.

[1] H. Russell, R. Stewart, C. Prior, V.S. Oganessian, T.G. Gault and J.E. Lovett. DEER and RIDME Measurements of the Nitroxide-Spin Labelled Copper-Bound Amine Oxidase Homodimer from *Arthrobacter Globiformis*. (2021). [Manuscript submitted for publication].

Nanodiscs or not nanodiscs? Conformational plasticity of an ABC exporter in different environments probed by EPR

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ABC transporters are proteins that couple the energy deriving from the binding and hydrolysis of ATP to large conformational changes that enable substrate translocation across membranes. MsbA is a homodimeric ABC exporter that flips lipid A - the precursor of lipopolysaccharide (LPS) - across the cytoplasmic membrane and is therefore essential for the survival of *E. coli* [1].

In this study, we used spin-labeled nanobodies (i.e. specific single domain antibodies) as conformational reporters targeting MsbA. The advantage of using spin-labeled nanobodies relies in the possibility of investigating membrane proteins in different environments, from in vitro to in situ without the need of site-directed mutagenesis, as previously shown by our groups [2]. Ideally, to understand structure and dynamics of membrane proteins, they should be investigated in situ, namely in the context of the living cell. However, structural elucidation of membrane proteins mostly requires their extraction from the native membrane environment with detergents. Membrane mimics such as liposomes or nanodiscs serve as surrogates of the native lipid bilayer and are widely used for structural and functional analyses of membrane proteins.

Here we use DEER (Double Electron Electron Resonance) to reliably measure distances between pairs of Gd(III) spin probes introduced in a non-state-specific nanobody targeting the two nucleotide binding domains in the MsbA homodimer. Data obtained in detergents, proteoliposomes, nanodiscs and cellular membranes from *E. coli* and *L. lactis* during the catalytic cycle will be presented. Intriguingly, we found that nanodiscs, in stark contrast to all other environments, funnel one specific conformation of the apo state of MsbA. The EPR-derived structural findings in nanodiscs are corroborated by cryo-EM structures obtained on the same spin-labeled samples. Our results put into question the physiological relevance of insights obtained using MsbA reconstituted in nanodiscs. This funneling effect in the energy landscape of a protein might not be an isolated case, rather it may occur in proteins characterized by a large degree of heterogeneity and flexibility.

[1] J. P. Overington, B. Al-Lazikani, A. L. Hopkins, *Nat. Rev. Drug Discov.*, 2006, **5**, 993-996.

[2] L. Galazzo, G. Meier, M. H. Timachi, C. A. J. Hutter, M. A. Seeger, E. Bordignon, *Proc. Natl. Acad. Sci. U.S.A.*, 2020, **117**, 2441-2448.

Determining Amyloid Oligomerization with Standard and High-Field EPR

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Tracking amyloid aggregation is necessary to understand neurodegenerative disease processes. While the smaller aggregates, oligomers, are considered to be the most harmful, they are difficult to detect. Here we show that by 9, 95, and 275 GHz continuous wave EPR at room temperature this oligomerization can be followed. We prepared model peptides, the EZ peptides, containing 12-13 aminoacid-residues and the backbone-fixed TOAC spin label.[1] Three peptides were synthesized, with TOAC at the N-terminus, T0EZ, the middle, T5EZ and the C-terminus, T12EZ. The figure shows the three components of in the EPR spectra of T0EZ, as obtained from the simulation of the EPR spectra at 9 and 95 GHz, and the development of the components as a function of time,.

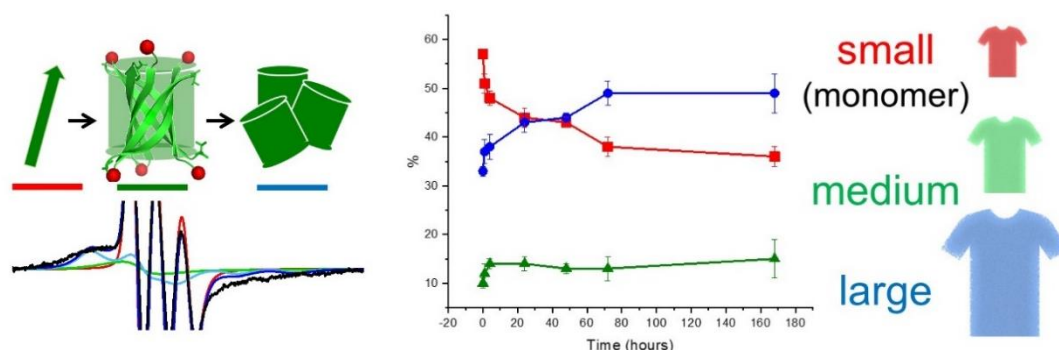


Figure 1

Extrapolating from this model, we expect that, in ideal cases, monomer resolution could be obtained. We have subsequently applied the approach to a protein related to Parkinson's disease, α -synuclein, showing that an oligomer can be detected that is invisible by standard methods.[2]

[1] E. Zurlo, I. Gorroño Bikandi, N. J. Meeuwenoord, D. V. Filippov and

M. Huber, *Physical Chemistry Chemical Physics*, 2019, **21**, 25187 – 25195

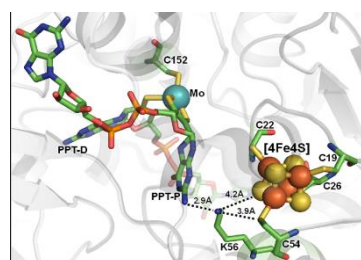
[2] E. Zurlo, P. Kumar, G. Meisl, A. J. Dear, D. Mondal, M.M. A. E. Claessens, T. P. J. Knowles, M. Huber, *PLOS ONE*, 2021, 0245548

Probing H-bond Network Changes in Molybdenum Enzymes Through EPR Analysis of Intercenter Magnetic Coupling

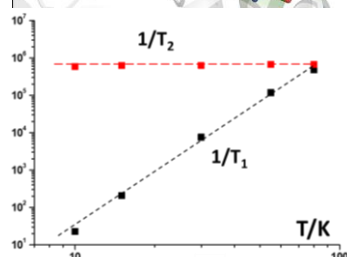
Bruno Guigliarelli,¹ Emilien Eteinne,¹ Kamal Zeamari,¹ Frédéric Biaso,¹ Guillaume Gerbaud,¹ David Pignol,² Monique Sabaty,² Pascal Arnoux,² Bénédicte Burlat,¹

¹Aix Marseille Univ, CNRS, BIP UMR7281, Marseille, France, ²Aix Marseille Univ, CNRS, CEA, BIAM UMR7265, Saint-Paul Lez Durance, France,

Molybdenum enzymes are present in virtually all living organisms where they are involved in a wide diversity of essential reactions. In prokaryotes, most of these enzymes carry a large Mo-*bis* pyranopterin guanosine dinucleotide cofactor (Moco) catalysing redox reactions associated with the transfer of two electrons and two protons [1]. Electrons are transferred to the Moco from the closest redox center which is usually a FeS cluster, and protons are exchanged with solvent through a series of protonatable residues or water molecules that connect the Moco to the surface of the enzyme. Enzyme activity results from a finely tuned combination of the catalytic process at the Moco and of the intramolecular electron and proton transfer processes. The catalytic efficiency can be regulated at these different levels and the molecular factors which control the enzyme reactivity are still largely debated. For instance, as for other complex oxidoreductases [2], gated proton transfer could be at work in such regulations [3].



In periplasmic nitrate reductase NapAB, we have shown that strong alterations of the enzyme activity could arise from modifications distant from the active site [4]. To understand the nature of these changes we have performed a detailed analysis of the magnetic coupling between the Mo(V) ion and the proximal FeS cluster.



Based on relaxation time measurements carried out on a wide temperature range, EPR spectra simulations and HYSCORE spectroscopy, our results are interpreted in terms of H-bond network modifications around the Moco upon activation/deactivation of the enzyme. This reveals a gated intramolecular electron transfer process in the modulation of the enzyme activity and emphasizes the role

of the second coordination sphere of the Mo ion in this mechanism.

[1] Grimaldi S, Schoepp-Cothenet B, Ceccaldi P, *et al*, *BBA-Bioenergetics*. **2013**, 1827, 1048

[2] Cui C., Greene BL, Kang G., Drennan CL, *et al.*, *J. Am. Chem. Soc.* **2021**, 143, 176

[3] El Attar S, Rendon J, Sidore M, *et al.*, *Submitted*, **2021**.

[3] Zeamari K., Gerbaud G., Grosse S, *et al.*, *BBA-Bioenergetics*, **2019**, 1860, 402.

Selective spin labelling of surface cysteines using a bromoacrylaldehyde spin label

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Structural investigations of proteins and their biological complexes are now frequently complemented by distance constraints between spin labelled cysteines generated using double electron-electron resonance (DEER) spectroscopy, via site directed spin labelling (SDSL). MTSL (methane thiosulfonate spin label), has become ubiquitous in the SDSL of proteins, however has some limitations. We introduce the use of bromoacrylaldehyde spin label (BASL) as a cysteine spin label, demonstrating a significant advantage over MTSL due to its increased selectivity for surface cysteines, eliminating the need to 'knock out' superfluous cysteine residues. Applied to the multidomain protein, histidine domain protein tyrosine phosphatase (HD-PTP), we show that BASL can be easily added in excess with selective labelling, whereas MTSL causes protein precipitation. Furthermore, using DEER, we were able to measure a single cysteine pair distance in a three cysteine domain, nine cysteine protein and ten cysteine protein complex.

Using a chimeric respiratory chain and EPR spectroscopy to determine the origin of semiquinone species previously assigned to mitochondrial complex I

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For decades semiquinone intermediates have been suggested to play an essential role in catalysis by one of the most enigmatic proton-pumping enzymes, respiratory complex I, and different mechanisms have been proposed on their basis. However, the difficulty in investigating complex I semiquinones, due to the many different enzymes embedded in the inner mitochondrial membrane, has resulted in an ambiguous picture and no consensus [1].

We re-examine [2] the highly debated origin of semiquinone species in mitochondrial membranes using a novel approach. Our combination of a semi-artificial chimeric respiratory chain, consisting of inverted membrane vesicles (submitochondrial particles, SMPs) supplemented with an alternative oxidase (AOX), with pulse EPR spectroscopy (HYSCORE) has enabled us to conclude, unambiguously and for the first time, that the majority of the semiquinones observed in mitochondrial membranes originate from complex III (Figure 1). We also identify a minor contribution from complex II.

We are unable to attribute any semiquinone signals unambiguously to complex I and, reconciling our observations with much of the previous literature, conclude that they are likely to have been misattributed to it. We note that, for this earlier work, the tools we have relied on here to deconvolute overlapping EPR signals were not available. Proposals for the mechanism of complex I based on the EPR signals of semiquinone species observed in mitochondrial membranes should thus be treated with caution until future work has succeeded in isolating any complex I semiquinone EPR spectroscopic signatures present.

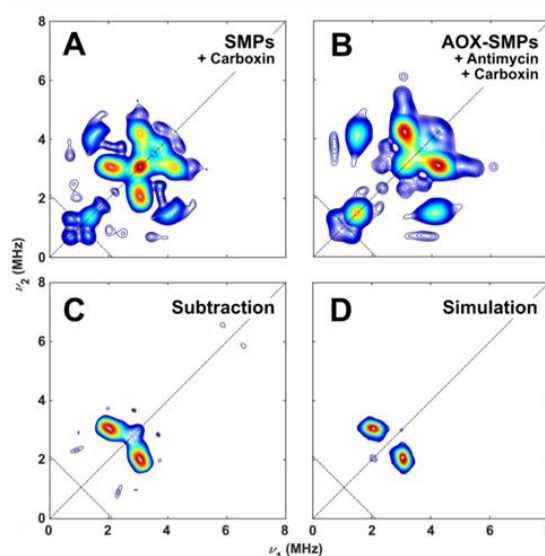


Figure 1. Comparison of ¹⁴N couplings in HYSCORE spectra of SMPs and AOX-SMPs at 40 K showing that the primary radical is from complex III.

[1] J. Hirst and M. M. Roessler, *BBA Bioenergetics* 2017, 1857 (7), 872.

[2] J. J. Wright, J. F. Fedor, J. Hirst, M. M. Roessler, *BMC Biology*, 2020, 18, 54.

Intracellular Protein-Lipid Interactions Studied by Rapid-Scan Electron Paramagnetic Resonance Spectroscopy

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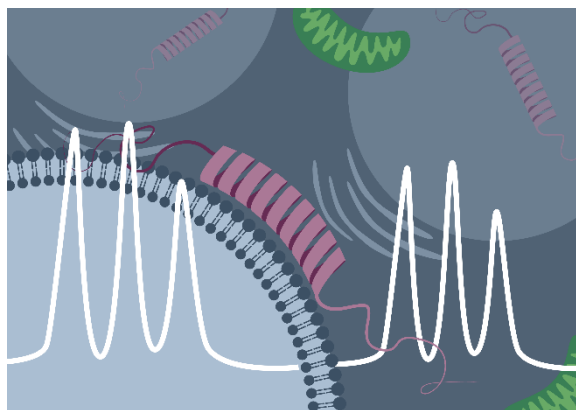
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[‡]These authors contributed equally.

Protein-membrane interactions play key roles in many intracellular processes, like signal transduction, vesicle formation and fusion. Alpha-synuclein (α S) is one prominent example of membrane-binding proteins, whereby its exact function is still unknown. Interaction with negatively-charged vesicles could be shown *in vitro*, but *in vivo*, no direct interaction could be detected so far, despite the high abundance of intracellular lipid membranes.

In this study we show for the first time rapid-scan (RS) electron paramagnetic resonance (EPR) spectroscopy in combination with spin-labelled proteins. We investigated the interactions of α S with negatively charged lipids and could detect lipid binding *in vitro* and upon transfection into oocytes of *Xenopus laevis*. Additionally, we could resolve the membrane-binding process in a time-dependent manner in the cellular environment. Our data hints towards a small fraction of α S interacting with endogenous membranes [1].



[1] T. S. Braun, J. Stehle, S. Kacprzak, P. Carl, P. Höfer, V. Subramaniam, M. Drescher, J. Phys. Chem. Letters, 2021, DOI: 10.1021/acs.jpclett.0c03583

Determining electron–nucleus distances and Fermi contact couplings from ENDOR spectra

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The hyperfine coupling between an electron spin and a nuclear spin depends on the Fermi contact coupling a_{iso} and, through dipolar coupling, the distance r between the electron and the nucleus. It is measured with electron-nuclear double resonance (ENDOR) spectroscopy and provides insight into the electronic and spatial structure of paramagnetic centers. The analysis and interpretation of ENDOR spectra is commonly done by ordinary least-squares fitting. Being an ill-posed, inverse mathematical problem, this is challenging, in particular for spectra that show features from several nuclei or where the hyperfine coupling parameters are distributed. We introduce a novel Tikhonov-type regularization approach that analyzes an experimental ENDOR spectrum in terms of a complete non-parametric distribution over r and a_{iso} [1]. The approach uses a penalty function similar to the cross entropy between the fitted distribution and a Bayesian prior distribution that is derived from density functional theory (DFT) calculations. Additionally, we show that smoothness regularization, commonly used for a similar purpose in double electron-electron resonance (DEER) spectroscopy, is not suited for ENDOR. We demonstrate that the novel approach can identify and quantitate ligand protons with electron-nucleus distances between 4 and 9 Å in a series of vanadyl porphyrin compounds.

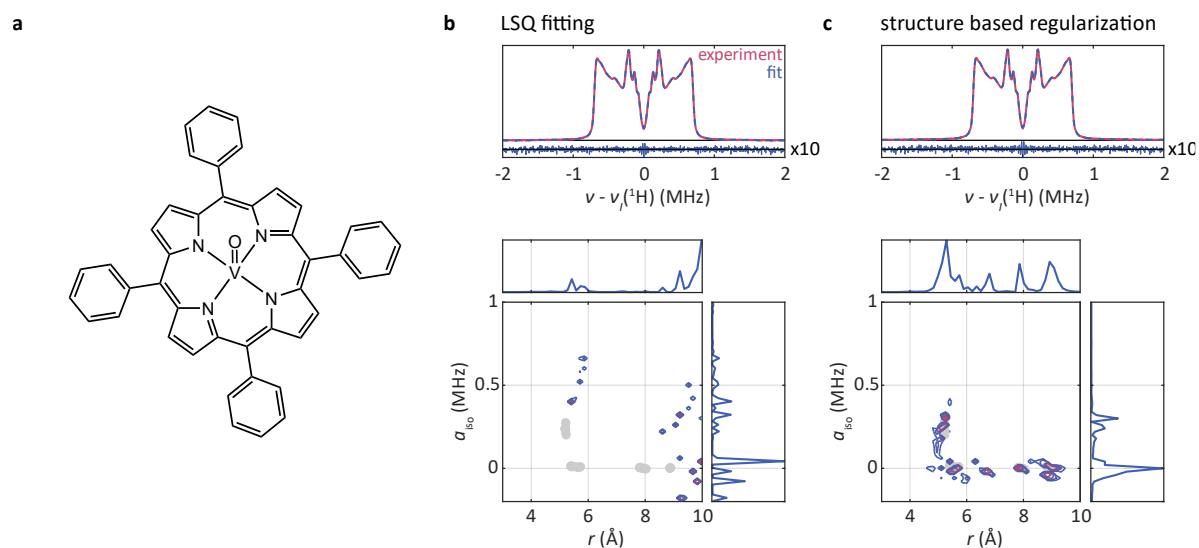


Figure 1: (a) Lewis structures of vanadyl tetraphenylporphyrin. Analysis of the ENDOR spectrum with the ordinary least square fitting (b) and the structure based regularization (c) approach. The top panels show the experimental spectrum, as well as the residuals with a magnification factor of 10. The bottom panels show the density distribution over distance r and contact coupling a_{iso} . DFT results are shown as gray dots.

[1] S. Pribitzer, D. Mannikko, S. Stoll, *Physical chemistry chemical physics: PCCP*, 2021, submitted.

Resolving small distance variations by single-molecule FRET & EPR spectroscopy using rotamer libraries

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Förster Resonance Energy Transfer (FRET) and Electron Paramagnetic Resonance (EPR) spectroscopy are complementary techniques that allow for quantifying distances in the nanometer range. Both approaches are commonly employed for probing the conformations and conformational changes of biological macromolecules based on site-directed fluorescent or paramagnetic labeling. FRET can be applied in solution at ambient temperature and thus provides direct access to dynamics, especially if used at the single-molecule level, while distance measurements by pulse EPR require immobilization or work at cryogenic temperatures but provide data that can be more reliably used to extract distance distributions. However, a combined analysis of the complementary data from the two techniques has been complicated by the lack of a common modeling framework. Here, we demonstrate a systematic analysis approach based on rotamer libraries for both FRET and EPR labels to predict distance distributions between two labels from a structural model. Dynamics of the fluorophores within these distance distributions are taken into account by diffusional averaging (Fig. 1), which improves the agreement with experiment. Benchmarking this methodology with a series of surface-exposed pairs of sites in a structured protein domain reveals that the lowest resolved distance differences can be as small as ~0.25 nm for both techniques, with quantitative agreement between experimental and simulated transfer efficiencies within a range of ~0.045. Rotamer library analysis thus establishes a coherent way of treating experimental data from EPR and FRET and provides a basis for integrative structural modeling, including studies of conformational distributions and dynamics of biological macromolecules using both techniques.

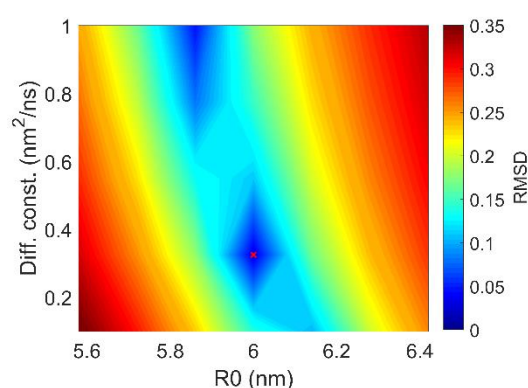


Fig. 1. FRET efficiency calculation in MMM2021 and root mean square deviation (RMSD) to experimental transfer efficiency, taking into account diffusional averaging of inter label distances.

The Potential of Pulsed Electron Spin Resonance for Tooth-based Retrospective Biodosimetry

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Large-scale triage after major radiological events, such as nuclear-reactor accidents or radiological terrorist attacks, requires a method of dose estimation called retrospective biodosimetry (RBD), able to detect doses in the range of 0.5–6 Gy. A well-known method for RBD is electron spin resonance (ESR), which can be used to detect and measure radiation-induced defects (stable free radicals) in the enamel layer of the teeth. The concentration of these defects is linearly correlated with dose in the applicable range. Despite its great potential, and proven results when applied to extracted teeth, ESR still struggles to provide accurate in-vivo readings. This is mainly because all available ESR-based RBD methods rely on quantitative signals for calculating the concentration of radicals in tooth enamel in order to evaluate the dose. This requires accurate knowledge of the volume of the measured enamel—not a viable option in live subjects. This study examined radiation-induced paramagnetic defects in the enamel layer of human teeth using advanced pulsed ESR methods, with the ultimate goal of supporting the development of an innovative practical RBD device for in-vivo use. We used a variety of pulsed ESR techniques, such as ESR relaxometry, ESR monitoring of instantaneous diffusion, and dipolar ESR spectroscopy (Fig. 1), to better understand the spectroscopic and physical characteristics of these paramagnetic defects, as well as the distribution of defects in the enamel layer, their interaction with the enamel layer, and the interactions between them. Applying such pulse techniques to irradiated teeth is far from trivial due to constraints of small signal magnitude and short coherence times. The findings from these innovative techniques provide us with a better understanding of the characteristics of radicals in tooth enamel and may be used for the development of an RBD device to estimate spin concentration and evaluate dose *without prior knowledge of the measured enamel volume*.

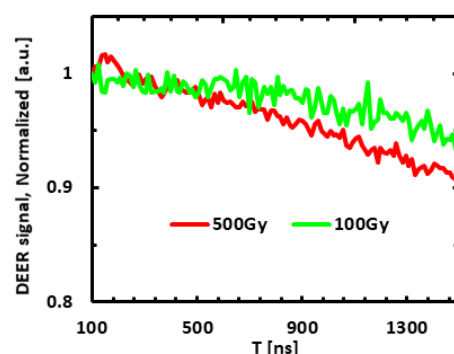


Figure 1: 3-pulse DEER signal of irradiated teeth with two different doses.

Investigating the elusive oxygen donor copper site within a protein type scaffold

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Here we report on the preparation and characterisation of a highly elusive Cu(II) binding site bound exclusively to oxygen donor atoms within a miniature artificial protein scaffold, a parallel three-stranded coiled coil, through an oxygen-rich binding site. Though originally designed for binding of lanthanides¹ (e.g. Gd(III)), the copper binding has been characterised by a range of spectroscopic techniques, and in particular EPR. EPR experiments with MB1-2 (Figure 1a) were able to unambiguously rule out nitrogen coordination as they found no evidence of either weakly coupled or directly bound nitrogen. The results were consistent with Cu(II) bound exclusively to oxygen donors, with evidence of directly bound water. EPR distance measurements using DEER and RIDME between bound Cu(II) and nitroxide radical spin label MB1-2_{TOAC} (Figure 1) further verified this assignment as comparison of the distance distributions reveal that both Gd(III) and Cu(II) appear to be binding at the same site. Despite coppers prevalence in biology and its affinity for oxygen donors, proteinaceous CuOx binding sites remain elusive. However, this technique demonstrates the power of a protein design approach to access chemistry not, to the best of our knowledge, exploited by biology.

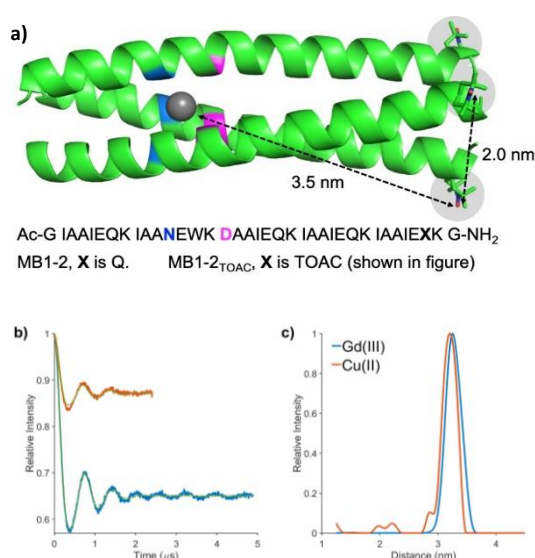


Figure 3: (a) Cartoon representation, rendered using ALLNOX, of models of the peptides studied in this work. The grey sphere is the proposed metal binding site. The predicted distances between a metal in the engineered binding site and the nitroxide radical of the TOAC spin label, and the inter TOAC distances, are presented. Four-pulse DEER experimental data for Gd(MB1-2_{TOAC})₃ (blue) and Cu(MB1-2_{TOAC})₃ (orange) showing (b) the time domain data after background correction and (c) the corresponding distance distributions. DEER experiments were performed at 10 K at Q-band and 15 K at X-band. Data were processed using DEERAnalysis2019.

[1] Berwick, M. R, et al (2014). De novo design of Ln(III) coiled coils for imaging applications. *Journal of the American Chemical Society*, 136(4), 1166–1169.

Interaction between 694nm red (ruby) laser photons and a static magnetic field – artefact or evidence for photon charge and mass?

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In 1997-8 I irradiated hair in an ESR spectrometer with a 694nm ruby laser [1]. I reported to the 2019 RSC-ESR conference a momentary 'off-resonance' of the microwave absorption at each pulse, during a scan at constant magnetic field to monitor the formation of a laser-induced radical; hypothesising that coherent photons in phase interacted with the magnetic field. Responding to a challenge that this could be an artefact due to temperature, I have further analysed the original data. The signal peak g value of laser-induced radicals was invariant with time in successive field scans, recorded at constant field and frequency. The hair in the sealed capillary melted. Melanin exhibits temperature-dependent paramagnetism when hydrated but not when frozen or dried as in hair [2]. If hair melts at 155 – 233°C, 6 – 10 J was absorbed or $2.2 - 3.6 \times 10^{19}$ red photons. The signal drop was 72% for 11 out of 15 laser pulses above the baseline in the time scan, giving a calculated field shift of 4 G or 4×10^{-4} T. The equation for the magnetic field B due to a moving point charge is:

$[\mu_0 = \text{magnetic permeability of free space } 4\pi \times 10^{-7} \text{ T m A}^{-1}, q = \text{particle charge and } v = c = \text{speed of light} = 2.998 \times 10^8 \text{ ms}^{-1}]$

$$\vec{B} = \frac{\mu_0}{4\pi} \frac{q\vec{v} \times \hat{r}}{r^2}$$

If the pulse is a point charge of $(N_{\text{photon}} \cdot q_{\text{photon}})$ with N_{photon} the number of red photons, and q_{photon} the photon charge, and r is 1 m, the field shift during laser firing might be expressed:

$$B_{\text{shift}} = 0.0004 = 4\pi \times 10^{-7} (4\pi)^{-1} N_{\text{photon}} \times q_{\text{photon}} \times 2.998 \times 10^8 \quad \text{or} \quad q_{\text{photon}} = \frac{0.0004}{(N_{\text{photon}} \times 29.98)}$$

For $2.2 - 3.6 \times 10^{19}$ red photons, the calculated charge is 6.1×10^{-25} to 3.6×10^{-25} coulombs. The electron charge is 1.6×10^{-19} coulombs thus the electron to red photon charge is $2.6 - 4.4 \times 10^5$. $E = h\nu = mc^2$ gives a mass of 3×10^{-36} Kg for red photons of frequency 4×10^{14} Hz. The electron mass is 9×10^{-31} Kg and the ratio of electron mass to red photon mass is 3×10^5 . I continue to propose this observation is not an artefact but evidence for a massive, electric charged and magnetic photon.

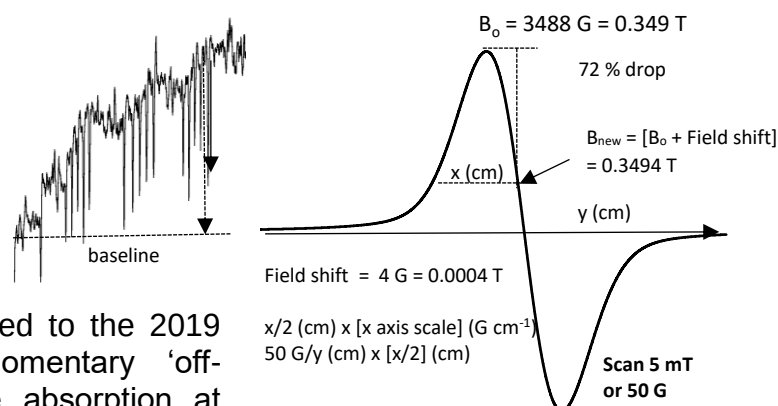


Fig. 1 Simulated spectrum of laser-induced radicals using centre field 348.8 mT; signal centre 349 mT; microwave frequency 9780 MHz; sweep width ± 2.5 mT; line width 0.81 mT; $g = 2.0014$; Lorentz/Gauss ratio 50/50. The percentage drop on laser firing was calculated from the time scan (inset) as the distance relative to the baseline (dotted line) of the 'off resonance' line.

[1] Rachel M. Haywood and Claire Linge. Differences in Production of Melanin Radicals by 694 nm Ruby Laser and UVA Radiation. *Lasers Surg Medicine* 2004, 35: 77-83.

[2] Chio SS, Hyde JS and R.C. Sealy. Temperature-Dependent Paramagnetism in Melanin Polymers. *Arch Biochem Biophys* 1980, 199: 133-139.

How do we separate a seemingly inseparable background?

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Interpretation of dipolar EPR spectroscopy results obtained from techniques such as multi-pulse DEER, RIDME, etc., relies on an accurate analysis of their associated dipolar signals. For this, we require robust estimation of the model parameters, such as the underlying distance distribution, modulation depth, spin concentration, etc.

A challenging aspect of dipolar EPR spectroscopy data analysis is separating the foreground and background contributions to the signals. This is particularly problematic when the amount (trace length) and quality (noise level) of experimental data are limited. Under these conditions, fits will yield multiple parameter sets (modulation depth, spin concentration, and distance distributions) that fit the experimental data equally well (see example in Figure 1). One common symptom of this is the appearance of false peaks at longer distances in the distance distributions and considerable uncertainty in the fitted parameters.

This phenomenon is known as non-identifiability, a dangerous source of uncertainty, which cannot be fully captured by most standard uncertainty quantification methods and poses a challenge to interpretability and robustness of results if ignored. We discuss the sources of non-identifiability and its diagnosis. We also present multiple strategies to restore identifiability, such as a new penalty, to ensure a unique separation of the background and the foreground in dipolar signals.

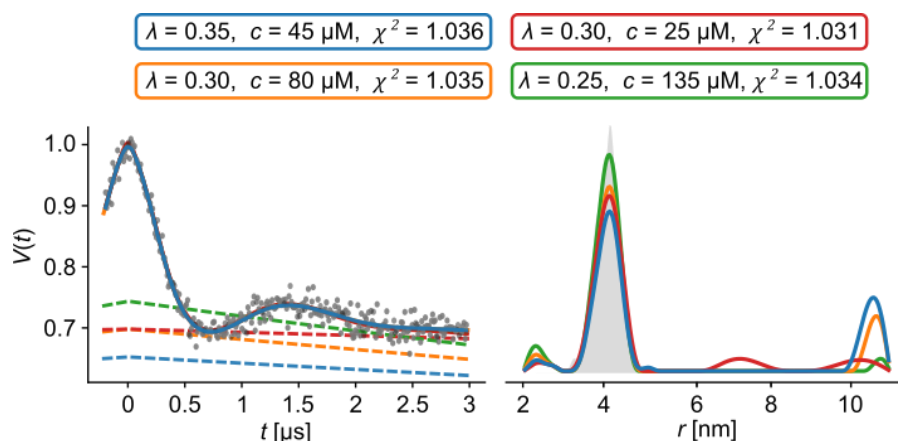


Figure 4: Example of non-identifiability of the background model and distance distribution during the analysis of a 4-pulse DEER signal. Different sets (indicated as colours) of modulation depth λ , pump spin concentration c and (right) distance distributions $P(r)$ lead to (left) different backgrounds (dashed) but equal signal fits (solid) of the experimental data (dots), as indicated by the χ^2 values.

DEERNet: how does it actually work?

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The signalling between inner layers of fully connected neural networks is scrambled because back-propagation training does not require perceptrons to be arranged in any particular order. The input and the output inherit the order from the training database, but all internal signalling has the appearance of noise. The resulting lack of interpretability and trust is a much criticised feature of deep neural networks.

We recently found a group-theoretical procedure that brings the intermediate signalling into a human-readable form [1]. Applied to magnetic resonance data processing networks, the method revealed unexpected internal sophistication: DEERNet (an EPR data processing network [2]) spontaneously invented bandpass filters, notch filters, frequency axis rectifiers, frequency division multiplexing, spectral filtering regularisation, and a transform that maps harmonic functions into Chebyshev polynomials [1].

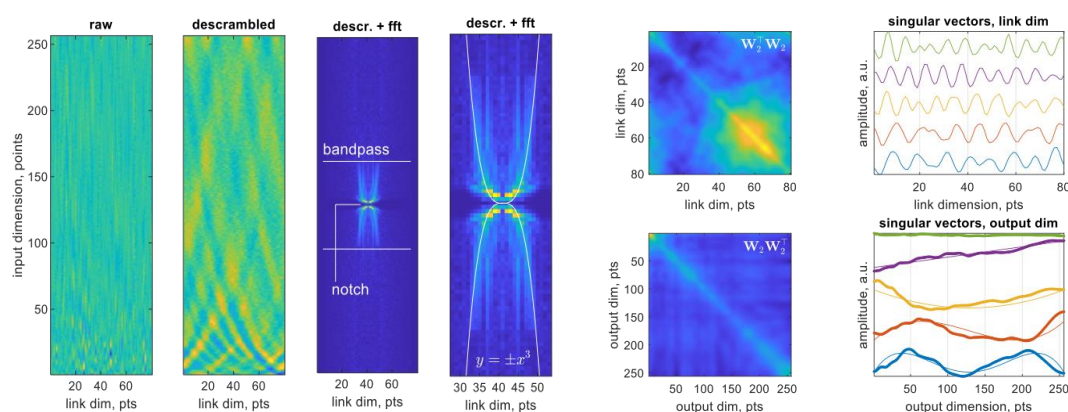


Figure 1. (left) Spontaneous emergence of a sophisticated digital filter in the input layer of a DEERNet [2] neural network. From left to right: raw weight matrix of the input layer, descrambled weight matrix, symmetrised absolute value 2D Fourier transform of the descrambled weight matrix, and a zoom into the central portion of that Fourier transform with a cubic curve overlaid. The layer applies a low pass filter to remove high-frequency noise, a notch filter at zero frequency to remove the non-oscillatory baseline. **(right)** Spontaneous emergence of a Fourier-like time-frequency transform, frequency division multiplexing and Chebyshev polynomials in the output layer of a DEERNet [2] neural net. Descrambling the link dimension reveals an approximately orthogonal (top left panel) conjugate signal library that singular value decomposition shows to be distorted sinusoids. SVD reveals spontaneous emergence of distorted Chebyshev polynomials (bottom right panel).

An ironic observation is that the act of interpreting the inner working of a neural net apparently obviates the need for it: the same filters and transforms may now be applied deterministically. Because the descrambler group approach [1] does not depend on the size of the network, this will likely extend to larger and more complicated cases.

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Tyrosine and Tryptophan Radicals EPR Spectra Simulation - TRSSA on the EasySpin platform

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A method of finding Hamiltonian parameters for simulation of tyrosyl radical CW EPR spectra was suggested in 2004 [1]. The name for the method, TRSSA (Tyrosyl Radical Spectra Simulation Algorithm), was coined a bit later [2]. The key feature of the algorithm was in the fact that the 40+ parameters required for a Tyr radical spectrum simulation were constrained by empirical formulas so that only two input variables were to be varied. A similar algorithm for tryptophanyl radicals [3] was named TRSSA-W (Tryptophanyl Radical Spectra Simulation Algorithm). From that point, we started referring to the original Tyr radical algorithm as TRSSA-Y, to distinguish the Tyr and Trp algorithms. The algorithms were working with the EPR spectra simulation software SimPow [4] that required a text input file to be generated by Excel for every new simulation.

Here, we report the two algorithms transferred onto the EasySpin [5] platform which makes the use of the algorithms much easier and also allows fitting routines while optimising parameters.

We will present examples of use of both algorithms as well as the method of reviewing several simulations, which is a strong complimentary method to the approach of automated parameters optimisation through mathematical criteria.

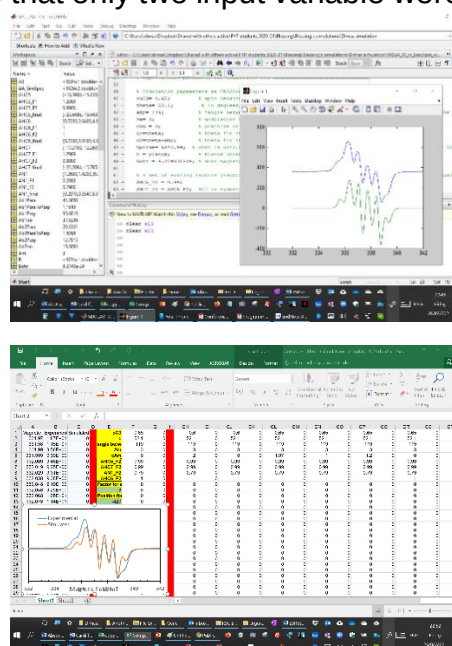


Figure 1. Simulation in MATLAB and review of the simulations in Excel.

[1] Svistunenko, D. A.; Cooper, C. E., A new method of identifying the site of tyrosyl radicals in proteins. *Biophys J* 2004, **87** (1), 582-595.

[2] Svistunenko, D. A., *Biochim Biophys Acta* 2005, **1707** (1), 127-155.

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[5] Stoll, S.; Schweiger, A., *J Magn Reson* 2006, **178** (1), 42-55.

Two-Dimensional Reconstruction of Distance Distributions in Double Electron-Electron EPR Spectroscopy via Singular Value Decomposition

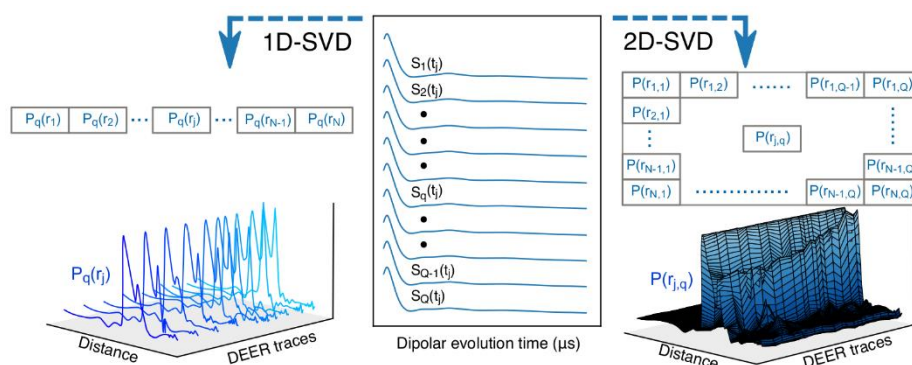
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Pseudo two-dimensional DEER experiments, such as T₁ or T_m-edited DEER allow to distinguish distance populations of interexchanging biomolecular systems and hence allow for leaps in structure biology, however their analysis remains treacherous [1,2]. Here we introduce the 2D Srivastava-Freed Singular Value Decomposition (SF-SVD) inversion method to permit independent and local refinement of the distances while collectively normalizing the 2D distributions to maintain its scale and attain measurable population changes. The 2D-SVD approach (Figure; right panel) returns the distance surface $P(r_{j,q})$ of which individual solutions to $S_q(t_i)$ are embedded on the surface; therefore 2D-SVD commutes the distance component in the time dimension as well as the traces dimension resulting in a gain in distance resolution compared 1D-SVD [3]. We demonstrate the approach on the analysis of T_m-edited DEER traces of protein A labeled with the R1 or R1p nitroxide to compare the addition of protons in a deuterated background to either leucine or phenylalanine, which subsequently allow for assignment of two otherwise indistinguishable DEER distance distributions.



[1] T. Schmidt, G. M. Clore, Chem. Commun. 56, 10890–10893 (2020).

[2] J. H. Wonderen, D. N. Kostrz, C. Dennison, F. MacMillan, Angew. Chem. Int. Ed Engl. 52, 1990–1993 (2013).

[3] M. Srivastava, J. H. Freed, J. Phys. Chem. A 123, 359–370 (2019).

S/N additivity of Integral Mellin transfer as way to improvement of PDS experimental scheme

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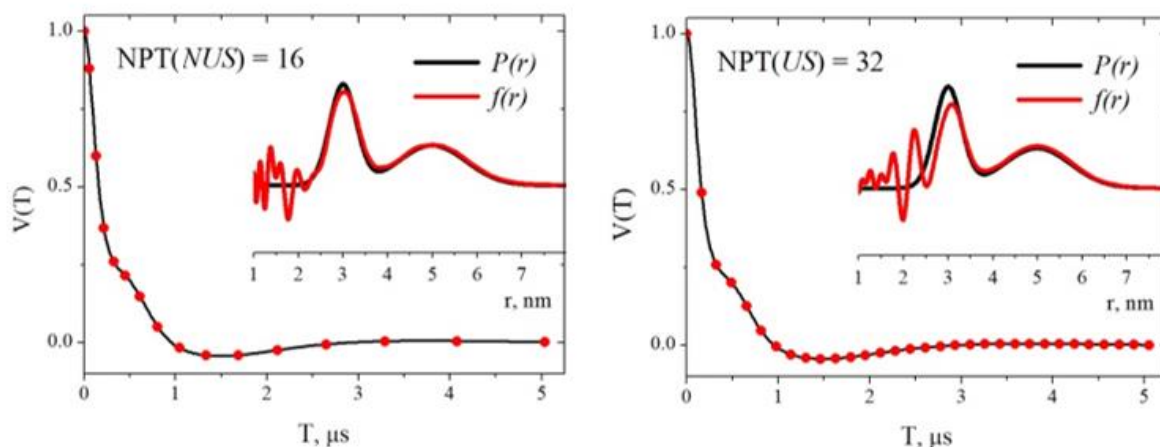
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Pulse dipolar spectroscopy (PDS) in Electron Paramagnetic Resonance (EPR) is a method of choice for determining the distance distribution function $P(r)$ for mono-, bi- or multi- spin-labeled macromolecules and nanostructures. Experimentally the signal $V(T)$ is measured by PELDOR, DEER, RIDME, SIFTER, DQC, etc. A well-known challenge for this set of methods is the ill-posed nature of reverse problem: extracting $P(r)$ from the measured $V(T) = \int_0^\infty P(r)\varphi(r,T)dr$

Many works demonstrate the efficiency of general mathematical methods to solve this inverse problem. But recently we introduced a new approach based on the specific form of the PDS kernel $\varphi(r,T) = \varphi(T/r^3)$ which allows separation of the variables r and T by an integral Mellin transform in an approach we call MeTA [1]. This approach has the unique property of additivity, i.e., the signal $V(T)$ and noise are uncoupled in MeTA (similar to the Fourier transform in NMR, ESEEM and HSCORE):

$$V(T) + Noise(T) = \int_0^\infty f(r)\varphi(r,T)dr \text{ and } f(r) = P(r) + Noise'(r)$$

This additivity lets us see how noise $Noise(T)$ propagates for data acquisition schemes with non-uniform sampling NUS or uniform acquisition US.



The figure shows improved efficiency of NUS: 16 points gives better fidelity between $P(r)$ and $f(r)$ than does US with 32 uniformly sampled points.

[1] A.G. Matveeva, V.M. Nekrasov A.G. Maryasov, *PCCP*, 2017, **19**, 32381.

Simulation of nitrogen nuclear spin magnetization of liquid solved nitroxides

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Nitroxide radicals are widely used in Electron Paramagnetic Resonance (EPR) applications. Nitroxides are stable organic radicals containing N-O group with hyperfine coupled unpaired electron and nitrogen nuclear spins. In the past, much attention was devoted to studying nitroxide EPR spectra and electron spin magnetization evolution under various experimental conditions. However, the dynamics of nitrogen nuclear spin was not investigated in detail so far. In this work, we performed quantitative prediction and simulation of nitrogen nuclear spin magnetization evolution in several magnetic resonance experiments. Our research was focused on fast rotating nitroxide radicals in liquid solutions. We used a general approach allowing us to compute electron and nitrogen nuclear spin magnetization from the same time-dependent spin density matrix obtained by solving the Liouville/von Neumann equation [1]. Especially we want to emphasize our prediction of a large dynamic nuclear polarization of nitrogen upon nitroxide irradiation with microwaves and influence of nitrogen nuclear spin dynamics on the nitroxide EPR saturation factor [2,3].

[1] Abragam, A., *Principles of Nuclear Magnetism*, Oxford University Press, 2011.

[2] Sezer, D., Gafurov, M., Prandolini, M. J., Denysenkov, V. P., & Prisner, T. F., *Phys. Chem. Chem. Phys.*, 2009, **11**, 6638–6653.

[3] Neugebauer, P., Krummenacker, J. G., Denysenkov, V. P., Parigi, G., Luchinat, C., & Prisner, T. F., *Phys. Chem. Chem. Phys.*, 2013, **15**, 6049.

Room Temperature Coherent Control of Spin Defects in hexagonal Boron Nitride

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Optically active defects in solids with accessible spin states are promising candidates for quantum information and sensing applications. To realize this, a coherent manipulation of their spin state is essential. While several candidates in 3D crystals including diamond and silicon carbide have been extensively studied, the coherent control of defects in 2D materials is still an open issue. The most prominent spin defect in 2D is the negatively charged boron vacancy (V_B^-) in hexagonal boron nitride (hBN). Its spin-triplet ($S=1$) ground state can be spin-polarized optically, which makes it attractive for optically detected magnetic resonance (ODMR). In our work¹ we realized a coherent control of these defects for the very first time by applying pulsed ODMR protocols. We measure spin-lattice relaxation time (T_1) of 18 μs and spin coherence time (T_2) of 2 μs at room temperature. T_1 increases by three orders of magnitude at cryogenic temperature following a $T^{-5/2}$ power law, while T_2 remains unaffected. Employing electron spin-echo envelope modulation (ESEEM) we separate the quadrupole and hyperfine interactions with the surrounding nuclei. By applying a multi-frequency "hole-burning" technique, we decouple the spin state from its inhomogeneous nuclear environment and extend the spin coherence time by a factor of three ($T_2^{\text{HB}}=7.5 \mu\text{s}$). Our results are important for employment of hBN as a high-resolution quantum sensor for hybrid quantum systems including van der Waals heterostructures, nanoscale devices and emerging atomically thin magnets.

[1] A. Gottscholl, M. Diez, V. Soltamov, C. Kasper, A. Sperlich, M. Kianinia, C. Bradac, I. Aharonovich and V. Dyakonov. *Sci. Adv.*, in press, 2021. arXiv preprint arXiv:2010.12513, 2020

Room-temperature formation of coherent spin pairs at silicon dangling bonds

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Electronic transport properties of semiconductors play a major role in solid-state physics and are efficiency-limiting for semiconductor-based devices like solar cells (SCs). In state-of-the-art silicon SCs [1], hydrogenated amorphous silicon (a-Si:H) layers are employed as charge-selective contacts. The device efficiency is crucially impacted by the transport properties of the crystalline-Si/a-Si:H interface. The disordered nature of a-Si:H produces a high density of localized states acting as charge traps or recombination centers. In its role as the prototypical amorphous semiconductor, transport via these disorder-induced states has been intensely studied for more than five decades. Despite this vast amount of research, however, fundamental questions remain unanswered concerning the nanoscopic nature of the major disorder-induced transport mechanisms.

Here we focus on recombination via dangling-bond (DB) defects, the primary charge-carrier loss mechanism at room temperature. We study operating a-Si:H SCs by electrically detected magnetic resonance (EDMR), the tool of choice to selectively probe transport channels through paramagnetic states. The DB recombination mechanism is commonly explained by the capture of a trapped electron into a DB defect, predicting an EDMR signature comprising the resonance lines of both spin states. Combining room-temperature multifrequency pulsed EDMR experiments with density-functional-theory (DFT), we show that instead a doughnut-shaped spin-pair complex forms prior to recombination. Within this complex the electron adapts its g -tensor to that of the DB, resulting in the observation of only the DB resonance. Surprisingly, we observe no indication of strong dipolar or exchange interaction, despite a localization of about 1 nm, which is confirmed also by DFT. Theory further predicts a relaxation of the paired spin complex in energy by over 0.2 eV, which is consistent with a spin-coherence time $T_2 \approx 1 \mu\text{s}$. The observation of this novel spin-pair complex thus not only requires a modification of the theory on transport and recombination in a-Si:H, but also provides a long-lived coherent spin state at room temperature with potential applications in the field of quantum computing.

[1] K. Yoshikawa et al., *Nat. Energy*, 2017, **2**, 17032.

Blatter Radical-Grafted Mesoporous Silica studied by EPR: Long Electron Relaxation Times and Opportunities for Spin Manipulation at Ambient Conditions

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Quantum computing and quantum information processing (QC/QIP) draw a lot of attention in physics, chemistry and materials science, and a lot of research has been done in this field using EPR. The main challenges include the development of suitable quantum bits (qubits), as well as methods of their manipulation [1]. Most qubit candidates known to date are designed for operation at low temperatures and are not applicable at ambient conditions. In this work we propose radical-grafted mesoporous silica as a prospective nanoplatform for spin-based QC/QIP up to a room temperature [2].

Different types of qubits have been already developed, e.g. paramagnetic centers in silicon, NV and other centers in diamond, quantum dots, paramagnetic metal complexes, etc. However, each of these solutions has one or more drawbacks requiring further developments. We introduce a new type of material into this field – mesoporous silica with organic (Blatter-type) radicals grafted onto its inner surface. The detailed pulse and CW EPR studies revealed the following advantages of this approach:

(i) The observed electron spin decoherence time T_m is sufficiently long to provide time window for quantum operations at ambient conditions; Rabi nutations were readily detected in a broad range of mw power. $T_m = 2.3 \mu s$ was obtained for the most dilute sample, and the trend in the series assumes possibilities for further increase of T_m . Such long T_m is ascribed to the nature of Blatter radical and nuclear spin-free composition of host material. (ii) The Blatter-type radicals are known to be extremely stable, and mesoporous silica host is an additional protector and stabilizer of these radicals against reducing agents and aggressive surroundings. (iii) The mesoporous structure of the studied materials opens up new possibilities to influence electron spins by embedding guest molecules into the channels and, more intriguing, designing new spin structures by means of added guest molecules.

This work was supported by RFBR (№ 20-53-12005) and DFG (FR 1372/26-1).

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Quantum Phase Interference in a Fullerene-Based Electron Triplet Molecular Qutrit

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High spin magnetic molecules are promising candidates for quantum information processing because their intrinsic multiplicity facilitates information storage and computational operations. However, due to the absence of suitable sublevel splittings, their susceptibility to environmental disturbances and limitation from the selection rule, the arbitrary control of the quantum state of a molecular electron multiplet has not been realized. Here we exploit the photoexcited triplet of C₇₀ as a molecular electron spin qutrit with pulsed electron paramagnetic resonance. We prepared the system into 3-level superposition states characteristic of a qutrit and validated them by the tomography of their density matrices. To further elucidate the coherence of the operation and the nature of the system as a qutrit, we demonstrated the quantum phase interference in the superposition. The interference pattern is further interpreted as a map of possible evolution paths in the space of phase factors, representing the quantum nature of the 3-level system.

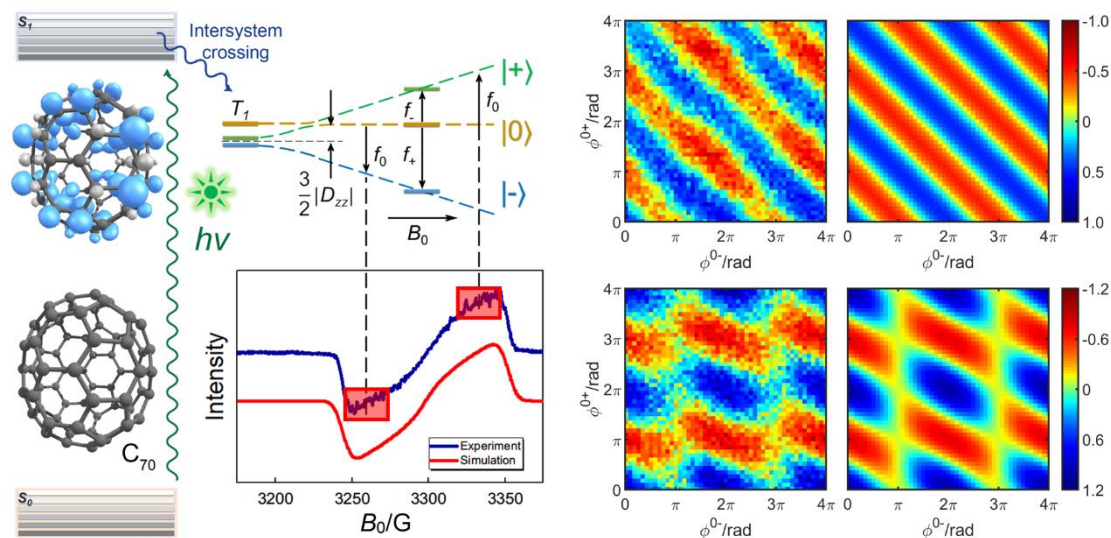


Figure 1. The excited triplet state of C₇₀ is treated as a qutrit, where the 3-level superposition state is prepared and characterized as quantum phase interference.

[1] Y.-X. Wang, Z. Liu, Y.-H. Fang, S. Zhou, S.-D. Jiang, S. Gao, *npj Quantum Inf.* **2021**, 7, 32.

Light-Induced Triplet–Triplet Electron Resonance Spectroscopy

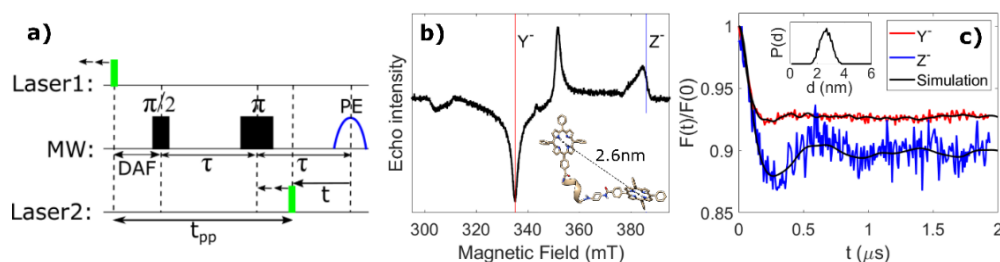
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The suitability of the porphyrin photoexcited triplet state for nanometre distance measurements by ESR Pulse Dipolar Spectroscopy (PDS) was demonstrated in combination with nitroxide radicals. Thanks to its non-Boltzmann population, the photoexcited triplet enhanced signal intensity when used as detection spin in PELDOR [1] and improved modulation depth when used as pump spin in LaserIMD [2]. Here we present the new technique of Light-Induced Triplet–Triplet Electron Resonance spectroscopy (LITTER) [3], which uses photoexcited triplet states as both detection and pump spins (a), enabling both the distance and angular distributions between the two triplet moieties to be determined. This is demonstrated for a model bis-porphyrin peptide ((b) inset) which renders dipolar traces with strong orientation selection effects (c). Using simulations and DFT calculations, we extract distance distributions ((c) inset) and relative orientations of the porphyrin moieties, allowing the dominant conformation of the peptide in frozen solution to be identified. LITTER removes the requirement of current light-induced PDS techniques to have a permanent paramagnetic moiety, becoming more suitable for in-cell applications and potentially giving access to distance determination in unmodified macromolecular systems containing photoexcitable moieties. LITTER also has the potential to enable direct comparison with FRET and combination with microscopy inside cells.



(a) LITTER sequence. (b) Echo-detected ESR spectrum of the bis-porphyrin peptide after photoexcitation. (c) LITTER traces (red and blue) and fits (black) leading to the distance distribution.

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[2] C. Hintze *et al.*, *J. Phys. Chem. Lett.* 2016, **7**, 2204-2209.

[3] A. Bertran *et al.*, *J. Phys. Chem. Lett.* 2021, **12**, 80-85.

Magnetic Edges and Coherence in Molecular Graphene Nanoribbons

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Graphene represents a well-defined two-dimensional honeycomb network of carbon atoms, which shows impressive electrical and mechanical properties [1]. Quasi-one-dimensional nanoribbons of graphene have emerged particular interest. By introducing magnetic edges in graphene nanoribbons, for instance, ferromagnetic couplings and superior spin filtering are predicted [2,3], making them candidates for future spintronic devices. Conventional techniques such as unzipping of carbon nanotubes, however, do not deliver the necessary degree of purity to design such systems.

Via an ultra-clean synthetic bottom-up approach, we were able to create graphene nanoribbons with great purity [4]. We were furthermore able to functionalize the ribbon edges with magnetic nitronyl-nitroxide radicals and Cu-porphyrin molecules, which serve as spin sites. Via electron paramagnetic resonance spectroscopy, we gain a comprehensive picture of the interactions between the magnetic radicals and the nuclei. The coherence time reaches microseconds at W-band frequencies at liquid nitrogen temperature. Using a combination of continuous-wave and time-resolved DEER spectroscopy, we obtained evidence of the existence of a magnetic edge state in the nanoribbon [5] and unravel its interactions with nuclei. We show HYSORE spectroscopy results, which reveal interesting interaction patterns.

[1] Geim, A. K., Novoselov, K.S., Nat. Mater., 2007, **6**, 183-191.

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[3] Farghadan, R., Saffarzadeh, A., RSC Adv., 2015, **5**, 87411.

[4] Narita, A., et al., Nat. Chem., 2014, **6**, 126-131.

[5] Slota, M., et al., Nature, 2018, **557**, 691-695.

Very High Sensitivity EPR – The HIPER upgrade

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One of the grand challenges in EPR is to improve the concentration sensitivity and time resolution of pulsed EPR measurements, and these were the core goals behind the previous development of a 94 GHz spectrometer called HIPER that made use of a wideband kW EIK amplifier [1]. This system was able to offer very high concentration sensitivity that exceeded that of commercial high-power pulsed Q-band systems, and with a time resolution that permitted relaxation time measurements of T_1 's and T_2 's down to a few nanoseconds.

In this paper we describe recent and ongoing upgrades that have further significantly improved the capability and sensitivity of this spectrometer.

We will outline upgrades in the detection system, signal processing, sample holders, and the novel integration/implementation of a coherent AWG system that permits full amplitude and phase control at 94 GHz, that can now fully exploit the available 1 GHz excitation and detection bandwidth.

Compared to the previous system, we will demonstrate advances that can improve concentration sensitivity further by more than an order of magnitude, and open up the possibility of routine wideband pulsed EPR measurements at sub- μm concentrations, using common spin labels. We will give examples showing full coherent excitation/detection of a 500 MHz broad nitroxide spectrum, and high sensitivity wideband PELDOR measurements of Gd, Mn and nitroxide spin systems that we believe demonstrates state-of-the-art performance.

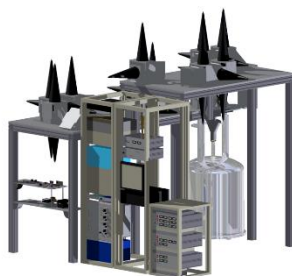


Figure 1. The 94 GHz kW pulsed HIPER spectrometer. The “witch’s hats” are high performance loads that help to eliminate standing waves in the system.

[1] P. A. S. Cruickshank, D. R. Bolton, D. A. Robertson, R. I. Hunter, R. J. Wylde, and G. M. Smith, *Review of Scientific Instruments*, **80**, pp 103102, 2009

A sensitivity leap for X-band EPR using a probehead with a cryogenic preamplifier

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Inspired by the success of NMR cryoprobes, we present an upgraded X-band EPR probehead, equipped with a cryogenic low-noise preamplifier. Our setup suppresses source noise, can handle the high microwave powers typical in X-band pulsed EPR, and is compatible with the convenient resonator coupling and sample access found on commercial spectrometers [1]. Our approach allows standard pulsed and CW EPR experiments to be performed with significantly increased sensitivity compared to the unmodified setup. The probehead demonstrates a voltage signal-to-noise ratio (SNR) enhancement by a factor close to 8x at 6 K, and remains close to 2x at room temperature. We reveal the full potential of this setup by demonstrating such SNR improvements using a suite of typical hyperfine and dipolar spectroscopy experiments on exemplary samples (Figure 1).

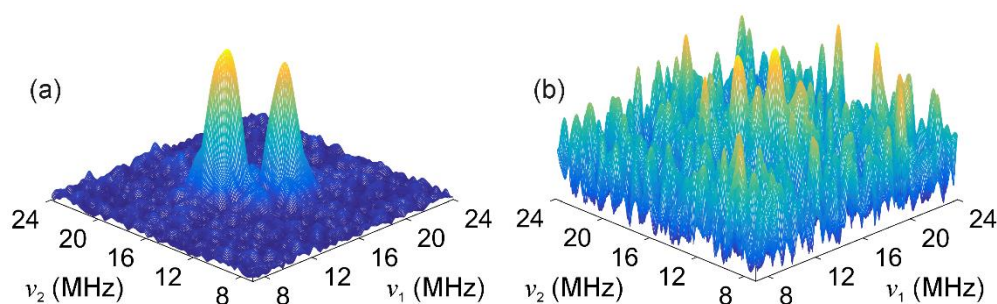


Figure 1. ¹H HYSCORE spectra of *Bos taurus* complex I measured using (a) upgraded and (b) standard setups.

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YBCO microresonators with ~50pL mode volume for high sensitivity EPR

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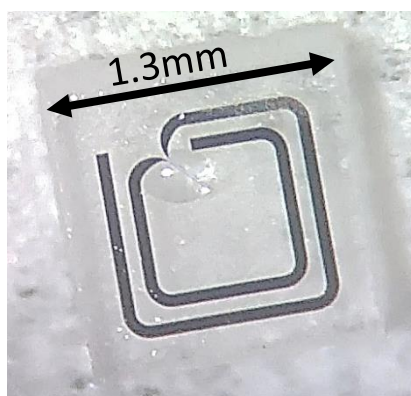
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We present microresonators fabricated from YBCO, a high critical temperature, high critical field superconductor. We show these resonators operate in a broad temperature range (up to 80 K) and field range (up to 1 T, limited by our magnet) and retain coupling limited quality factors above 1000 except at the highest temperatures. These resonators achieve higher Q (and thus sensitivity) than microresonators made of normal metals [1] despite containing micron-scale (6 μm) features, 100x smaller than previous YBCO resonators [2]. The high operation temperature and field contrast with microresonators made of elemental or binary superconductors (e.g., Nb, NbN, TiN). Our resonators are fully compatible with commercial spectrometers and may be loaded into spectrometers similarly to 'normal' samples either in a sample tube or on the end of a Teflon rod.

We use these YBCO resonators to measure example systems in CW and pulsed EPR at X-band frequency. Example systems include both solid and liquid samples and have both inorganic and biological origin typical of a range of common EPR experiments. We investigate the effect of resonator design upon critical EPR parameters such as maximum inversion fraction and π -pulse duration. We show improved inversion efficiency using adiabatic fast passages. We measure samples much larger than our mode volume containing $\sim 10^{10}$ spins and calculate a spin sensitivity of $< 10^8$ spins. Using these microresonators, we perform pulse experiments such as HYSORE on protein samples.



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Rapid Scan Electron Paramagnetic Resonance with EPR-on-a-Chip Sensors

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Electron paramagnetic resonance (EPR) spectroscopy is the method of choice to investigate and quantify paramagnetic species in e.g., semiconductor devices, proteins, catalysts, and molecular magnets. Common EPR spectrometers use large electromagnets and microwave (MW) resonators with high quality factors (Q), thus limiting their application for *in situ* and/or *operando* measurements, which are of particular interest in materials research. Here, we present an improved design of a miniaturized EPR spectrometer implemented on a silicon microchip (EPR-on-a-chip, EPRoC). Instead of the typical resonator and microwave bridge, the EPRoC sensor uses an array of planar coils, each with a diameter of 200 μm , each of which is part of a voltage-controlled oscillator (VCO). Thereby, the VCO array both acts as MW source and EPR detector. The individual VCO elements provide an excellent spin sensitivity, which is extended by the VCO array for improved concentration sensitivity. Moreover, thanks to their working principle, the VCOs offer the possibility to sweep the MW frequency without limitations caused by the resonator Q. Frequency-swept experiments allow the use of smaller, permanent magnets rather than bulky electromagnets required for field-swept EPR. Frequency sweeps with scan rates up to 2,000 THz/s combined with intrinsically high B_1 of 0.5 mT render EPRoC ideal for rapid frequency scan EPR. RS-EPR can yield signal-to-noise improvements, especially for samples with long relaxation times relative to scan rate, which would otherwise be saturated in continuous-wave EPR [1]. In this contribution, we review the recent advances in RS-EPRoC measurements and demonstrate improvements in both SNR and spin sensitivity by two orders of magnitude for similar signal acquisition times, compared to continuous wave (CW-EPRoC) using a grain of the α,γ -Bisdiphenylen- β -phenylallyl complex with benzene (1:1) as sample. An outlook for future EPRoC designs will be presented, discussing possible sensitivity improvements via faster sweep rates and larger B_1 capabilities.

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High Frequency ESR: New Tools for Investigating Thin Layers of Molecular Magnets

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Molecular Magnets (MM) are molecular systems susceptible to the application of magnetic fields. Their properties are appealing for high-density information storage (Single Molecule Magnets, SMM) [1] as well as for quantum information processing (Molecular Spin Qubits, MSQ).[2,3] The easiest way to realize devices based on these emerging technologies is to deposit and incorporate thin layers of MM on surface. With this aim, new methods have been introduced to access structural, magnetic and dynamic information of thin layers of MM. Electron Spin Resonance spectroscopy (ESR) at conventional frequencies is a fundamental tool for bulk and thin layer samples. When moving to High Frequency ESR (>100 GHz), measurements of thin layer samples are precluded because of sensitivity. Here, we present a 2D resonator for HF-ESR based on plasmonic metasurfaces. This resonator focuses the THz magnetic field in a confined area, which results in ESR signal enhancement when dealing with 2D samples. Thanks to plasmonic metasurface resonators, HF-ESR enters among the tools for the investigation of MM on surface.[4] This work is part of the FET-OPEN PETER project, whose main purposes will be briefly outlined within the talk.[5]

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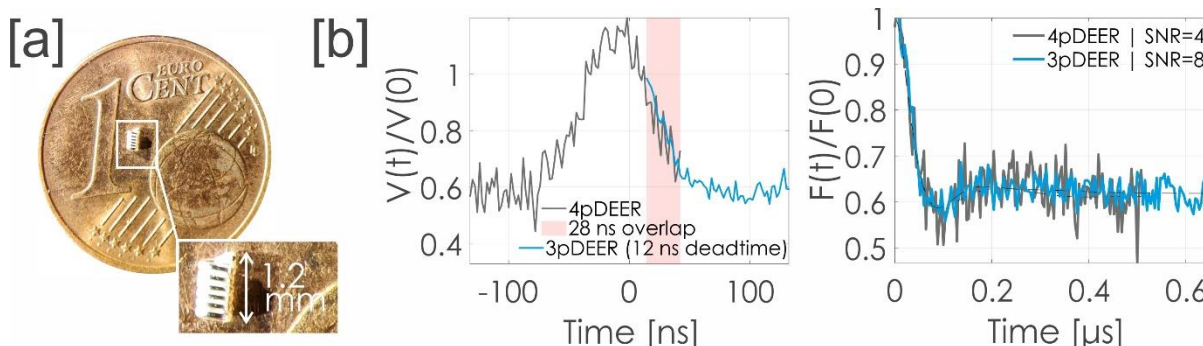
[5] www.peter-instruments.eu

Milliwatt DEER on fast relaxing spin species

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Pulse electron paramagnetic resonance (EPR) experiments rely on very high incident microwave powers (> 300 W) to create the short pulse lengths needed to excite a sizeable portion of the spectrum. However, such high powers result in long deadtimes (> 50 - 100 ns) which limit the applicability of pulse EPR. In order to significantly reduce the power needed for these experiments, superior B_1 -conversion efficiencies Λ are required. The recently introduced microhelix [1] combines a high B_1 -conversion efficiency ($\Lambda = 3.2$ mT/W^{1/2}) with a good B_1 -field homogeneity over the sample and an intrinsically large bandwidth (low Q-value) of 100 MHz when critically coupled. We report deadtimes down to 12 ns achieved using only 300-600 mW of power at X-band. Small build sizes, as realized with the microhelix shown in [a], give access to volume-limited samples, while shorter deadtimes allow to investigate fast relaxing spin species. In order to take advantage of this setup, deadtime-limited experiments were explored. We show that the deadtime-limited 3-pulse DEER experiment offers superior sensitivity over the 4-pulse DEER experiment in case of fast transverse relaxation times [b]. In addition, microhelix resonators pave the road towards low-cost and yet sensitive benchtop cw/pulse EPR spectrometers, which will accelerate the adoption of pulse EPR by a broader community [2].



[a] Size comparison of the microhelix (0.4 mm inner diameter; 1.2 mm height) [1] and a one Eurocent coin (16.25 mm diameter). **[b]** 3-pulse (12 ns deadtime) and 4-pulse DEER experiments performed with the microhelix. DEER-Stitch [3] can be utilized to combine 3-pulse and 4-pulse data to compensate for deadtimes in 3-pulse DEER. The SNR gain of performing a 3-pulse over a 4-pulse DEER is 200% at a T_m of 0.7 μ s.

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A chorus of chirps for broadband ESR spectroscopy

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Sophisticated spin manipulations in magnetic resonance are generally achieved by either composite pulses, frequency-modulated pulses, or pulses generated by numerical methods like optimal control theory. In ESR spectroscopy, considerable amount of work has been done to achieve broadband inversion and excitation over the wide range of ESR frequencies that can span over hundreds of MHz [1-3].

Frequency-modulated (also known as swept-frequency or chirped) pulses can offer ultra-broadband irradiation bandwidths. However, designing excitation schemes using these pulses, is more challenging than a single 90° hard pulse, and requires several chirped passages.

One such scheme is the CHORUS (Chirped Ordered Ultrabroadband Spectroscopy). Originally developed for broadband excitation of ¹⁹F spins in NMR spectroscopy [4, 5], this sequence, offers several advantages over its counterpart, the Kunz-Bodenhausen scheme [6, 7]: a wider uniform excitation bandwidth, robustness to B_1 field inhomogeneities, and a shorter duration.

In this presentation the implementation and some applications of the CHORUS scheme in ESR spectroscopy [8] will be discussed, and theoretical background, simulated as well as experimental results will be presented.

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Accurate Determination of Exchange Interactions in Single-Chain Magnets and Other Multi-Spin Complexes by THz-EPR

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Exchange-coupled metal-metal and metal-radical complexes are crucial in (bio-) catalysis and molecular magnetism. Knowledge of their zero field splittings (ZFS) and exchange interactions are essential for their characterization. Frequency-domain Fourier-transform

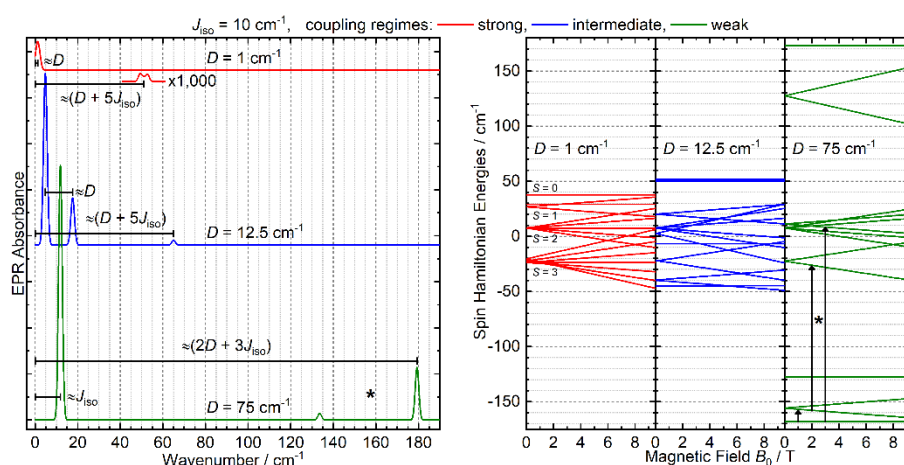


Fig. 1 Simulated frequency-domain EPR (left) and energy levels (right) for two FM coupled $S = 3/2$ representative for different coupling regimes.

(FD-FT) THz-EPR is ideally suited to study spin systems with interactions up to hundreds of wavenumbers. Although determination of dominant exchange interactions by EPR is typically not possible, as $\Delta S_t = 1$ transitions are forbidden, anisotropies from e.g. ZFS may grant them sufficient probability (Fig. 1). Thus, J couplings and ZFS can be simultaneously obtained, as we have demonstrated recently for multi-nuclear complexes. In a newly synthesized class of 1D Co^{II}-based, thiocyanate-bridged spin chains, some of which behave as single chain magnets (SCMs), intra- and interchain couplings could be provided [1-3]. In addition, we determined the local ZFS of the Co^{II} ions from transitions to the second Kramers doublet (asterisk in Fig. 1) for the first time in such spin chains [4]. Tensor anisotropies and orientations could be obtained based on the combination of simulations and *ab initio* theory. Implications of these findings for SCM properties will be discussed alongside examples of further multi-spin systems.

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High-field EPR as a structural method for copper(II)-nitroxide magnetic compounds

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Novel copper(II)-nitroxide magnetic materials $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ are able to change structural and magnetic properties under external stimuli such as temperature, pressure or light. This effect could be a foundation for the next generation of molecular data processing devices and sensors. Unique interactions in exchange-coupled CuO_6 octahedral spin centers lead to bistable behavior. Namely, many of $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ compounds feature two possible spin states with distinct geometries, magnetic and physical properties. One of the big advantages of copper(II)-nitroxide compounds is that their organo-metallic polymer molecular structure results in high plasticity of the crystals and their high structural diversity comparing to classic SCO compounds. Use of different nitroxide radical substitutes and polymer chain motifs often leads to entirely new features of the magnetostructural transition.

In this work we describe new copper-nitroxide polymer chain compound $\text{Cu}(\text{hfac})_2\text{L}^{\text{MeMe}}$ exhibiting unique two-step magnetostructural transition. Complex approach includes XRD, SQUID, FTIR and EPR study of the compound. However, high structural changes make $\text{Cu}(\text{hfac})_2\text{L}^{\text{MeMe}}$ crystals break below the lower step of the transition at 40 K. As a result, XRD data is not available for the low-temperature state of the compound, complicating comprehensive description of the transition. To describe the low-temperature state we used high-field EPR (30 T, 693 THz) with impulse magnetic field. Interestingly, in the experiment, ~30% of $\text{Cu}(\text{hfac})_2\text{L}^{\text{MeMe}}$ crystals orient along the magnetic field. The remaining 70% stays in unorient powder form. The effect is clearly seen on EPR spectra and allows to obtain key structural features of the low-temperature state. We were able to calculate relative orientations of magnetic centers of $\text{Cu}(\text{hfac})_2\text{L}^{\text{MeMe}}$ and find direction of the Jahn-Teller axis elongation of exchange-coupled triad center just from the powder EPR spectrum of the compound.

Acknowledgements

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Easy-Plane to Easy-Axis Anisotropy Switching in a Co(II) Single-Ion Magnet Triggered by Diamagnetic Lattice

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Single ion magnets (SIM) are promising unit blocks for ultra-dense data-storage devices and quantum computers. The prerequisite for SIM behaviour is large zero-field splitting (ZFS), an intramolecular property. In addition, intermolecular electron spin interactions can strongly influence the macroscopic magnetic properties of SIM bulk materials. Magnetic dilution of paramagnetic samples by complexes with diamagnetic ions is a routinely used approach for disentangling the inter- and intramolecular electron spin interactions. Yet, as will be shown herein, magnetic dilution, may not only change intermolecular interactions, but also intramolecular properties, determining SIM behavior.

We studied the magnetic properties of the SIM $[\text{Co}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2]$ along with its magnetically diluted analogues with the general formula $[\text{Co}_x\text{Zn}_{(1-x)}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2]$ by XRD, X-band and THz-EPR spectroscopy, AC magnetic measurements and quantum chemical calculations (QCC). THz-EPR [1] allowed for direct determination of large ZFS in $[\text{Co}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2]$ and its Zn-diluted analogues down to 10% of Co(II) content. The ZFS was found to be almost constant in the range between 100% to 50% of Co(II) content. However, it drastically decreases from $\sim 75 \text{ cm}^{-1}$ to $\sim 50 \text{ cm}^{-1}$ while decreasing the Co(II) content below 50%.

The reason for this shift can be rationalized with the help of dilution dependent XRD analyses. XRD showed that dilution with Zn does not only change the average distance between paramagnetic ions, but induces also structural changes at the remaining Co sites. This indicates that $\text{Co}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2$ molecules can be found in one of two geometries which correspond either to Co(II) or Zn(II) lattice. Further evidence could be obtained by QCC, which unveiled that the dilution-induced structural transition in $\text{Co}_x\text{Zn}_{(1-x)}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2$ leads to spin levels inversion of Co(II) ion forming true-SIM spin levels order. This observation was reliably confirmed by X-band EPR and AC magnetometry. The latter also allows one to determine the magnetic relaxation pathways for Co(II) ion spin system in both types of $\text{Co}(\text{piv})_2(2\text{-NH}_2\text{-Py})_2$ geometries.

S.L.V. thanks the Russian Science Foundation (17-13-01412) for support of this work.

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Reversible control over spin and charge dynamics of paramagnetic dopants in Ti(IV)-based oxide nanocrystals

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One long-standing challenge in spintronics and quantum information processing is the design of new materials with tunable electron spin properties and dynamics. We combine synthetic chemistry with myriad of structural and spectroscopic techniques to study Ti(IV)-based oxide nanocrystals with tunable carrier densities that possess substitutional magnetic dopants. In our initial efforts we found that the choice of precursor and its controlled hydrolysis play a vital role in the successful dopant incorporation. This key finding enables the successful doping of colloidal nanocrystals of SrTiO₃, BaTiO₃, and TiO₂ with an array of paramagnetic ions at substitutional Ti-sites. We further explored the interplay between dopants and photochemically-added excess electrons that localize at paramagnetic Ti³⁺ defects. Using variable temperature EPR spectroscopy, we observe drastic acceleration of the spin relaxation time of substitutional Cr³⁺ dopant ions with the incorporation of fast-relaxing Ti³⁺ defects through an efficient cross-relaxation process. While investigating the generality of the drastic dopant-defect interaction, we discovered that other dopants such as Fe³⁺ behave differently in the presence of Ti³⁺ and instead appear to reduce to the EPR-silent Fe²⁺ dopants. These results provide a new design strategy and ultrafast control over spin and charge states of localized paramagnetic centers in oxide semiconductors.

Synthesis Redox-active Perylene diimides for Battery Applications

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All organic redox flow batteries have attracted enormous scientific interest due to the flexibility of design and the renewability of resource of the active materials. perylene tetracarboxylic diimides (PDI) are known for their interesting electronic and optical properties making them promising candidates for such applications. This study details the synthesising approaches of redox active material using perylene dianhydride (PTCDA) as starting material. PTCDA molecules functionalised with different acid and amine groups at the imide-position such as 4-aminophenyl, neopentyl 4-aminobenzene sulfonate and 4-benzylphosphonic acid diethyl ester, as well as the functionalisation of the bay area with electron reach group which leads to interesting optical and electronic properties. It has been observed that introducing electron donating substituents at the bay region has large effects in terms of the compounds UV/Vis maxima and consequently their colour. It also shows significantly enhanced thermal and chemical stability as evidenced by TGA. The structures were successfully determined by single-crystalline X-ray diffraction analysis.

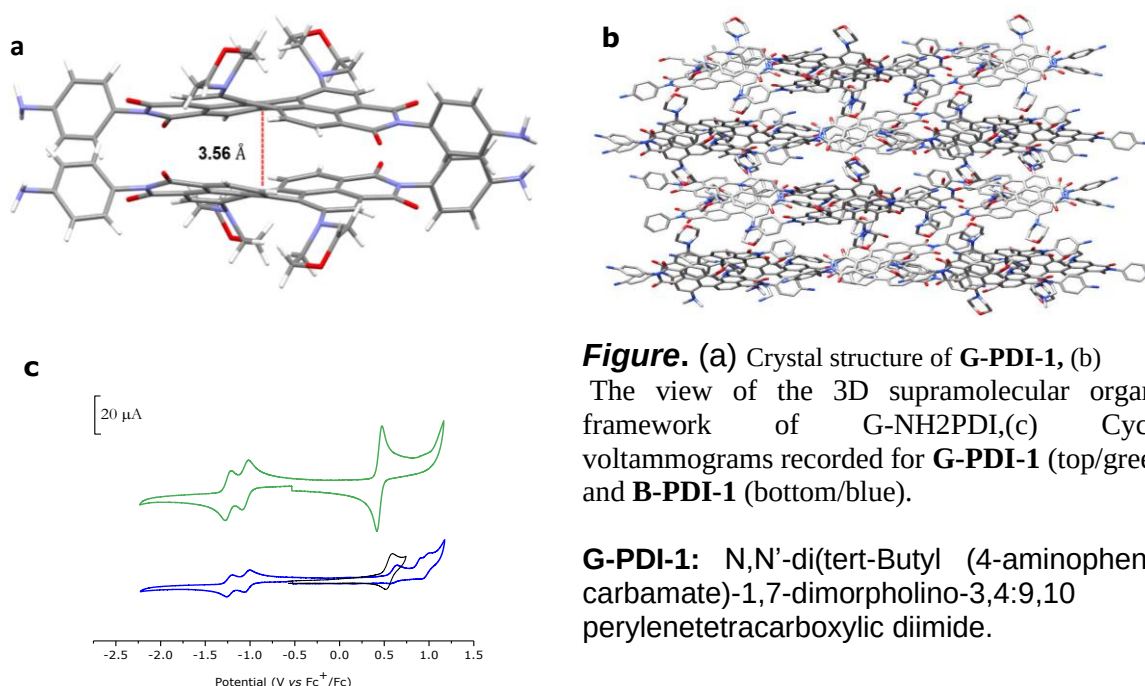


Figure. (a) Crystal structure of **G-PDI-1**, (b) The view of the 3D supramolecular organic framework of **G-NH₂PDI**, (c) Cyclic voltammograms recorded for **G-PDI-1** (top/green) and **B-PDI-1** (bottom/blue).

G-PDI-1: N,N'-di(tert-Butyl (4-aminophenyl) carbamate)-1,7-dimorpholino-3,4:9,10 perylenetetracarboxylic diimide.

Origin and reactivity of radical species in milled quartz and their evolution over time

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It is well known that industrial processing, including cutting, milling, and polishing, of quartz-containing materials, is a key step that elicits toxicity in silica dust.¹ During fracturing, the breakage of Si-O covalent bonds in silica yields highly reactive surface species that promptly react with surrounding molecules. Such reactions define the chemistry and bioactivity of the newly formed particle faces, during surface reconstruction process.² To understand how radicals created by fracturing quartz evolve into biologically relevant surface features, including specific populations of silanols recently proved to turn silica inflammogenic,^{1b} a systematic study of the radical species generated by fracturing quartz under different conditions and their evolution over time has been performed by CW-EPR. Ad-hoc prepared synthetic quartz crystals were fractured down to respirable size ($d_{90} < 10 \mu\text{m}$) in a ZrO_2 planetary ball-mill under Ar, H_2O vapour saturated Ar (ca. 27 torr H_2O), and ambient (ca 130 torr O_2 , ca. 7 torr H_2O) atmosphere. EPR spectra of fractured quartz were recorded immediately after milling. Radical kinetics were followed by storing fractured quartz under Ar, H_2O and molecular O_2 and the reactivity of surface sites elucidated. Thermal annealing was performed to evaluate the stability of the radicals in the bulk. This study shows that different radicals yielding different surface reconstruction pathways are obtained during milling in different environments. Radicals formed at quartz surface become stabilized in the bulk, where they act as a reservoir for further surface reactions with outer molecules.

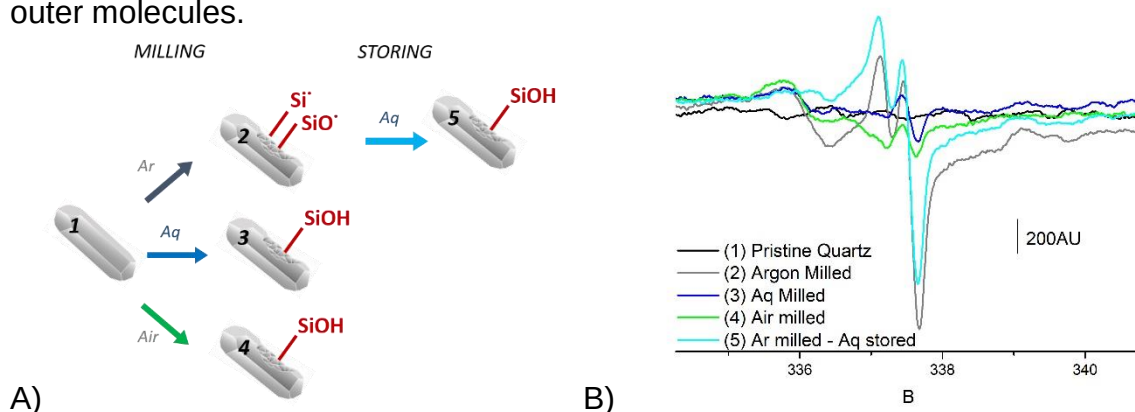


Figure 1: a) Schematic representation of milling and storing conditions of synthetic quartz used in this study and b) CW-EPR of pristine and milled in different atmospheres quartz dusts.

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Freeze quench: a practical approach

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In enzymatic catalysis, the development and optimization of methods for trapping and stabilizing short-lived reaction intermediates is in constant evolution, with the perspective of obtaining detailed mechanistic information of fast catalytic turnovers whose investigation is not possible with traditional techniques. In this scenario, rapid freeze-quench (RFQ) represents a powerful biophysical tool that allows the trapping of transient species at the milliseconds time scale[1]. In this project, RFQ is combined with electron paramagnetic resonance (EPR) spectroscopy to investigate the so-called Compound I, which is proposed as the common active intermediate in heme-peroxidases, catalases, chloroperoxidases and, under certain conditions, in P450 enzymes[2]. The spectroscopic study of Compound I is intended to get insights in the magnetic coupling scheme of this paramagnetic species, in order to draw a comprehensive picture of structure-function relationship in the enzymes of interest. RFQ-EPR experiments are supported by stopped-flow UV-vis spectroscopy, which provides essential kinetic data and allows the determination of individual reaction steps and relative rate constants. A practical overview of the experimental set-up is given. The binding reaction between myoglobin and sodium azide, whose kinetics is known[3], is used as model reaction for the calibration of the RFQ system. Preliminary results on selected peroxidases, such as chloroperoxidase (CPO) are also shown.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813209.

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Mapping Single-Metal Sites in Cu-CHA Zeolite with ^{17}O EPR: Structure and Dynamics

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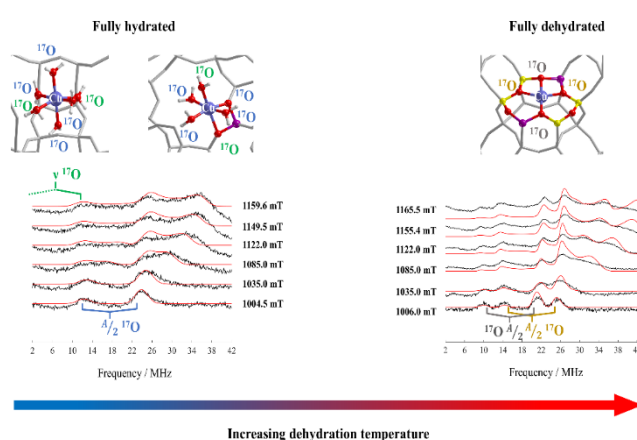


Figure 5. Experimental (black lines) and simulation (red lines) of Q-band ENDOR spectra recorded at 20 K of fully hydrated Cu-Chabazite (on the left) and fully dehydrated (on the right). The assignment of the ^{17}O signals is indicated on corresponding model

Copper-exchanged zeolites have been in the focus of comprehensive studies for decades and are a subject of evergreen interest in catalysis due to applications ranging from NO_x removal to the direct conversion of methane to methanol.[1,2] The high activity of copper-containing zeolites in oxidation and reduction reactions is typically related to the nature of metal-oxygen bonds. Such detailed information can be extracted from the hyperfine couplings of coordinating oxygen ions.[3,4] However, the only magnetic isotope of oxygen is ^{17}O but its natural abundance (0.037%) is by

far lower than the value required for the detection of hyperfine structure. By selective ^{17}O isotopic labelling of the zeolite framework, in conjunction with advanced EPR methodologies and DFT modelling, we recover the ^{17}O hyperfine interactions associated with Cu-O bonds. This enables to determine the local structure of single site Cu^{II} species and follow their dynamics as a function of hydration conditions.

This poster is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement no. 813209.

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Estimating Optical DNP Saturation Factors From Time-Resolved EPR Data

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Overhauser Dynamic Nuclear Polarization (DNP) is a popular method for improving the sensitivity of Nuclear Magnetic Resonance (NMR) spectroscopy in solution.¹ It is usually carried out by saturating the Electron Paramagnetic Resonance (EPR) transitions of a radical that is added to the sample, leading to nuclear hyperpolarization via cross-relaxation. However, the signal enhancements achievable are limited by the

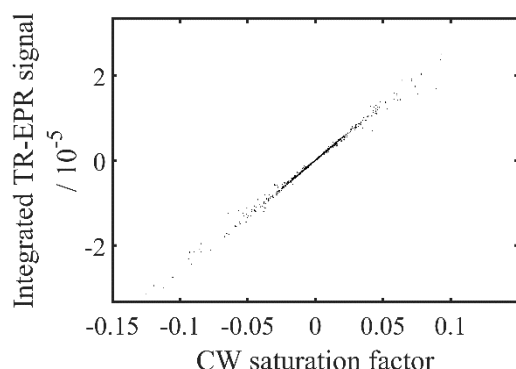


Figure 6: Scatter plot of the integrated TR-EPR signal versus CW saturation factor for randomly generated values of all triplet decay rate constants, the radical and dye concentrations, P_n , and T_{1e}

saturation factor, which has a maximum value of 1 in the case of complete electron spin saturation. It may be possible to overcome this limit through the use of electron spin hyperpolarization. It has been demonstrated that DNP can be optically induced in the absence of microwaves, with the radical becoming polarized following the quenching of photoexcited triplet states via the Radical-Triplet Pair Mechanism (RTPM).^{2,3} Although the initial water enhancements in the presence of the radical TEMPO and the dye rose bengal were promising, they were far from exceeding the theoretical limit of conventional DNP. Therefore, a number of

system parameters need to be optimized, such as dye and radical concentrations, laser power, RTPM polarization, triplet lifetimes, and electron spin relaxation rates. It would be hugely beneficial if such optimization could be carried out using the Time-Resolved EPR (TR-EPR) signals of the dye-radical system following pulsed laser excitation, without having to measure the DNP enhancements, thus allowing for rapid screening of potential polarizing agents. Here, I present theoretical investigations into establishing qualitative and quantitative links between the time-integrated TR-EPR signal and the continuous-wave saturation factor, including a study into the ranges of parameter space over which such links apply.⁴

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Electron spin polarization transfer induced by triplet–radical interactions in the weakly coupled regime^[1]

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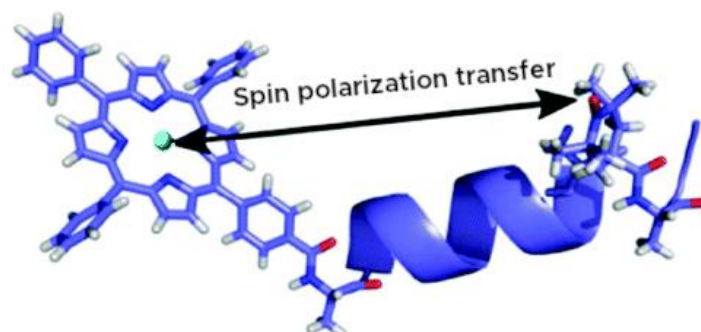
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An electron spin polarization transfer from a porphyrin triplet state to a weakly coupled nitroxide radical has been observed in a human neuroglobin (NGB) mutant. This mutant contains a Zn(II) protoporphyrin IX in substitution of its native heme prosthetic group and a nitroxide attached via site-directed spin labeling to the Cys120 residue. Transient EPR data show a net polarization gain for the triplet state of the Zn(II) protoporphyrin, attributed to the dynamic Jahn–Teller effect. The decay of the spin polarization of the triplet state is accompanied by the arising of a polarized EPR signal of the nitroxide. The experiment is compared to one performed on a synthetic polypeptide with free-base tetraphenylporphyrin and a nitroxide bound to it at 2.4 nm, the same distance as the spin labels in the NGB mutant. In the transient EPR spectrum of this molecule, neither a net polarization of the triplet state nor a polarization of the nitroxide species can be observed. This is attributed to the lower symmetry of the porphyrin that makes it not Jahn-Teller active. A perturbation theory treatment suggests that the radical polarization occurs by transfer of the net polarization of the triplet state. The effect has been studied in analogous synthetic polypeptides with a Zn(II)-tetraphenylporphyrin and a nitroxide label bound at different positions in order to investigate the dependence of the polarization transfer on the distance.



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Redox Noninnocent Behaviour of Nickel(II) Complexes with Hexaazamacrocyclic Ligands

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Base-metal complexes with ligand-centred radicals are of interest in multielectron catalysis inspired by metalloenzyme systems. The rational design of efficient catalysts of important chemical reactions requires an understanding of the structure and spectroscopic properties. A series of six nickel(II), copper(II) and palladium(II) complexes with hexaazamacrocycles H_2L^H and H_2L^{OMe} (Fig. 1) were synthesised and characterised by analytical, spectroscopic techniques, as well as by spectroelectrochemistry.^[1]

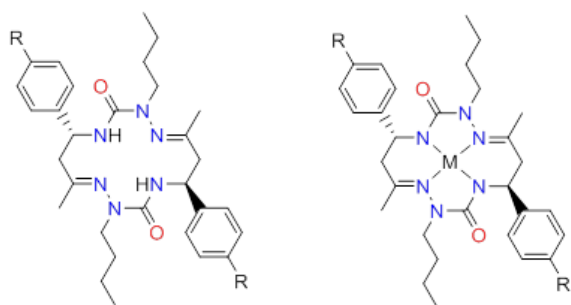


Figure 1. Proligands and complexes reported in this work. R = H or OMe; M = Ni, Cu or Pd.

The complexes contain low-spin nickel(II) and palladium(II), as well as copper(II) with $S = \frac{1}{2}$ in square-planar coordination environment. EPR spectroelectrochemical experiments and DFT calculations indicate possible tautomerism between nickel(III)–ligand and nickel(II)–ligand radical states for oxidised Ni(II) complexes, and so the strong noninnocent character of the ligands.^[1]

This work was supported by the Science and Technology Assistance Agency under the contracts no. APVV-15-0053, APVV-19-0024, and DS-FR-19-0035, by the Slovak Grant Agency VEGA under contracts no. 1/0504/20 and 1/0466/18, and by the STU Grant scheme for Support of Excellent Teams of Young Researchers.

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Micro-crystals and subnanoliter liquid samples measurements using surface micro-resonators

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Electron spin resonance (ESR) spectroscopy of paramagnetic species in single crystals and liquids is a powerful tool for sample characterization. Unfortunately, conventional ESR systems have limited sensitivity and are optimized for millimeter-size solid samples and ~1 ml liquid volume. Therefore, conventional ESR cannot measure many interesting materials in single-crystal form such as enzymes and inorganic catalytic materials (e.g., zeolites), which only form micron-scale crystals (1-200 μm). Furthermore, conventional ESR is not compatible with microfluidics methods, which typically involve the use of liquids with small volume (microliters to picoliters).

Here, we present a unique family of miniature surface resonators optimized for micron-scale single crystals and picoliter liquid samples. The devices' resonant mode(s) were characterized by ESR micro-imaging and compared to the theoretical calculations. Moreover, experimental ESR spectra of single microcrystals with typical sizes of ~25-50 μm and subnanoliter liquid samples are presented. Additionally, we show that microfluidic ESR makes it possible to apply huge (~1000 T/m) and fast (~1 μs) pulsed magnetic field gradients to the sample. This is a key capability to measuring unique properties such as nanoscale real-space diffusion and quantum spin diffusion. Microfluidics experiments were performed at room temperature, making our technique compatible with future microfluidics applications that might employ a full system of compact resonators, microfluidic chips, miniature magnets, and a compact ESR-on-a-chip spectrometer. This could result in a completely new approach to processing and measuring paramagnetic liquid samples for use in a variety of chemical, biological, medical, and environmental applications.

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Correlating Physical and Biochemical Properties of Membrane Proteins in Model Membrane Systems

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In mitochondria, respiratory complex I (R-CI) pumps four protons by transferring two electrons down an energy gradient from NADH, through a flavin mononucleotide and a chain of seven Fe-S clusters to ubiquinone (Q₁₀). The free energy produced by the redox reaction, which is used to transport protons across the mitochondrial inner membrane, builds the proton-motive force that is consumed to drive ATP synthesis [1,2]. While NADH oxidation and electron transfer through the Fe-S clusters are relatively well understood, the mechanism of Q₁₀ reduction remains unresolved, not least due to the extreme hydrophobicity of Q₁₀.

Our study analysed lipid vesicles with mammalian complex I (proteoliposomes, PLs), based on their colloidal properties to complement the established biochemical characterisation (see **Figure 7**) [3,4]. By applying dynamic light scattering (DLS) in combination with electrophoretic light scattering (ELS), the size, size distribution and zeta potential of the independent respiratory units were determined. In addition, spin-labelled fatty acid probes were incorporated into the self-assembled PLs to monitor how the size and fluidity of the boundary and bulk lipid phase are affected by the lipid composition of the liposomes using electron paramagnetic resonance (EPR). These techniques allow the correlation of these colloidal properties with protein retention and outward orientation as well as the specific activity of R-CI inside the PLs. This approach provides the potential to guide the preparation of such self-assembled artificial respiratory chains systematically and hence improve on the traditional trial-and-error based approach.

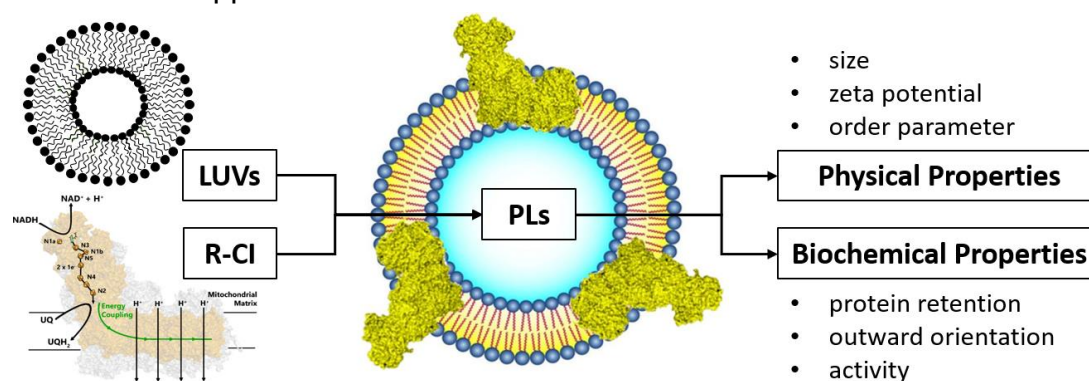


Figure 7 Preparation of proteoliposomes (PLs) of respiratory complex I (R-CI) based on large unilamellar vesicles (LUVs) and analysis of their physical and biochemical properties.

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EPSRC National Research Facility for EPR Spectroscopy

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Engineering and
Physical Sciences
Research Council



The University
of Manchester



The University of Manchester hosts the EPSRC National Research Facility (NRF) for EPR Spectroscopy, which accommodates several Bruker EPR spectrometers, with capabilities for CW (L-, S-, X-, K- and Q-band) and pulsed (S-, X- and Q-band) EPR measurements, electrochemical EPR and optical excitation, along with a Quantum Design MPMS3 SQUID magnetometer (DC, VSM and AC modes). This provides a unique research base for studying paramagnetic species and materials.

Support: The Facility can provide support for most experimental EPR techniques at multi-frequencies and variable temperatures; 1.6 K to 500 K (frequency dependent) with cryogen-free cryostats. Pulsed hyperfine expertise supports users in accessing ESEEM, ENDOR, EDNMR and HYSCORE methods. Pulsed Dipolar Spectroscopy (PDS) methods including DEER/PELDOR, RIDME, CIDME and Light induced methods are all supported. Advice about spectrum simulation and access to data modelling software is available.

Updates: The Facility has acquired a second X-band pulsed spectrometer, (adding to the X-band and S-/Q-band machines) and the ability to measure with a 1 GHz detection bandwidth at S-/Q-band. We also have a high sensitivity 3 mm QT-II resonator in combination with 150 W Q-band amplifier, ideal for low concentration biological samples. The SQUID magnetometer has optical access, oven (1000 K), sample rotation and ULF options. Upgrades for optical excitation will provide excitation across the range from 210-2400 nm *via* tuneable OPOs. A collaborative arrangement with Oxford University provides access to CW and pulsed EPR at 94 GHz.

Access: The Facility has continued to operate during the last two COVID-19 lockdowns and external samples can be measured through the EPR NRF; sensitive samples can be sent by dry shipper. Moving forward, opportunities for remote viewing, training and access to EPR experiments will be possible *via* shared desktops. ***If you are preparing a research proposal for a project that may require access to the Facility, please contact us for advice.***

Structural insights into the heme domain of, peroxxygenase-like cytochrome P450, CYP116B5hd

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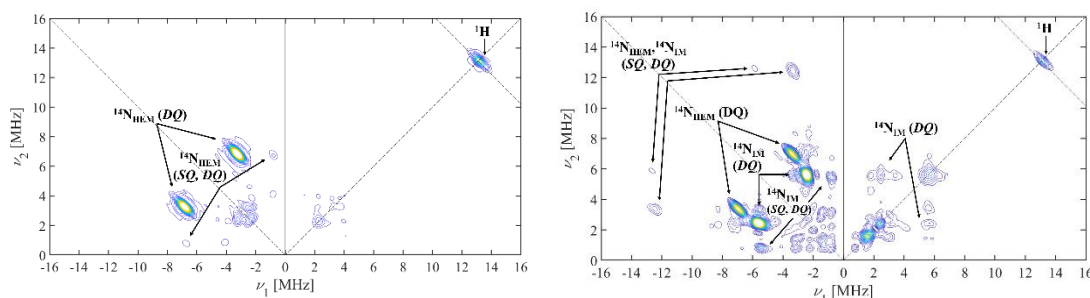


Figure 1. X-band HYSCORE spectra of CYP116B5hd with (right) and without imidazole (left).

The electronic structure of CYP116B5hd,[1] a peroxxygenase-like P450 cytochrome with high stability to hydrogen peroxide reactivity,[2] is studied by means of Continuous Wave (CW) and Pulse EPR techniques. The substrate-free protein shows the characteristic EPR spectrum of a low-spin ($S=1/2$) Fe^{III} -heme centre[3] of CYP450.[4] The local coordination environment of the Fe^{III} is further characterized by means of HYSCORE spectroscopy in both presence and absence of imidazole, providing a detailed description of the electronic structure of the metal 3d orbitals involved in metal–ligand bonding. Despite the similarity of the g -tensor with that of CYP450 monooxygenases, CYP116B5hd behaves as a P450 peroxxygenase, indicating that the electronic environment of heme iron is not the only factor determining peroxxygenase activity.

This poster is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813209.

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Photoactivation studies of Cr(I) complexes by EPR spectroscopy

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Linear α -olefins are a versatile class of organic molecules employed in a wide variety of industrial processes [1]. Among these, the most employed are 1-hexene, 1-octene, synthesized by oligomerization reaction with Chromium based catalysts. Chromium has access to a variety of oxidation states among these some contain unpaired electrons which makes them suitable to be studied by Electron Paramagnetic Resonance (EPR) spectroscopy. These complexes require an activation step which is normally performed by chemical activation with EtAl_3 or other Al based alkylating agents.

The complex $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]^+$ was investigated for photoactivation experiments using UV light [2]. All evidence collected so far has demonstrated that the radiation can break the Cr-C and Cr-P bonds, as had been expected from previous studies on Cr(0) complexes [3]. While the end product of this reaction $[\text{Cr}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2]^+$ is unlikely to have any catalytic activity two of the other species that are formed, *mer*- $[\text{Cr}(\text{CO})_3(\kappa^1\text{-dppp})(\kappa^2\text{-dppp})]^+$ and $[\text{Cr}(\text{CO})_2\text{dppp}(\eta^6\text{-arene})]^+$ are still being investigated [3].

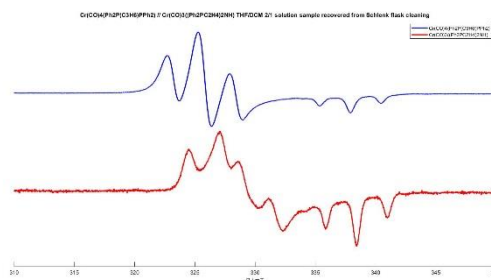


Figure 8: 140K cw-X band spectra of $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]^+$ and $[\text{Cr}(\text{CO})_3((\text{Ph}_2\text{P}(\text{C}_2\text{H}_4))\text{NH})]^+[\text{Al}(\text{OC}(\text{CF}_3)_4)]^-$

A variation on this system, $[\text{Cr}(\text{CO})_3((\text{Ph}_2\text{P}(\text{C}_2\text{H}_4))\text{NH})]^+$ was chosen in hopes that an extra coordination site with Nitrogen would prevent the ligand from detaching from metal centre. So far, EPR investigation of this complex has revealed that it reacts with UV light and that Cr-C bond breakage is likely occurring. Investigation on the chemical activation or catalytic activity is to be carried out in the following weeks.

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Conformational Changes in the Structure of Human Calmodulin in a Calcium-Substrate Dependant Manner

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Mapping and understanding the myriad interactions that occur within the regulatory networks that comprise the cellular proteome is key to our understanding of all cellular processes. To achieve this, tools such as Electron Paramagnetic Resonance (EPR) specifically Double Electron Electron Resonance (DEER) are being developed and adapted to perform measurements in the cellular environment. EPR and DEER are versatile techniques that enables the elucidation of protein function, interaction and three-dimensional topographical structure through the application of paramagnetic spin labels^{1,2}.

Human Calmodulin 1 (CaM1) is a protein ubiquitously expressed within all tissue in the human body. It provides a suitable target for refinement of in-cell EPR methodology due to the structural information already available as well as the different cellular pathways it is involved in. By understanding the range of function through conformational changes that are possible, the proteins that Calmodulin interacts with may be targeted or inhibited for the purposes of disease mediation and/or treatment. This work showcases measurements of structural changes using Double Electron-Electron Resonance (DEER) using a recombinant protein CaM1-M13 composed of Human Calmodulin 1 and the synthetic calmodulin-binding domain of skeletal muscle myosin light chain kinase (skMLCK). The structure ensures stable conformation of CaM1 around the M13 peptide enabling consistent distance measurements that can be compared to other structural permutations both in the presence and absence of calcium ions.

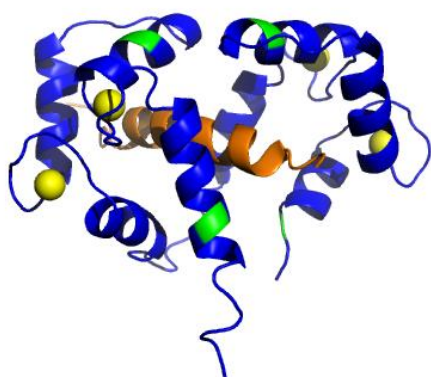


Figure 1. Calmodulin (Blue) wrapped around calmodulin-binding domain of skeletal muscle myosin light chain kinase complex (Orange) in the presence of calcium ions (Yellow). Four substituted cysteines for site-directed spin labelling (Green) surround the binding site, each on separate EF-Hand motifs.

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Enantiopure bridged triarylaminines heterohelicenes radical cations monolayer assembled on surface

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It has been observed that paramagnetic species can influence the magnetoresistance of a molecular-based spintronic device.¹ A similar spin filtering effect can be also achieved by exploiting the chirality of molecules. "CISS effect" (Chiral Induced Spin Selectivity),² opens the way to the possibility to employ a chiral molecule as spin filtering agent. In this respect, the family of hetero-helicenes has been recently identified as a promising candidate to control spin transport properties as they merge the characteristics of a chiral structure and radical properties in a unique compound and, further, they maintain all the advantages related to the use of purely organic molecule in molecular spintronics. In perspective to investigate these properties a fundamental step is represented by the development of an assembly procedure of molecules on surface. In this work we report the first successful attempt of depositing a chiral organic radical on surface maintaining the magnetic and structural properties of bulk phase. The deposition of thia[4]helicene radical cation³ (**Fig.1**) exploiting non-covalent interaction with the substrate was investigated by spectroscopic technique such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS). Besides, X-ray Natural Circular Dichroism evidenced the persistence of the chiral structure of the single layer of radicals assembled on surface.⁴

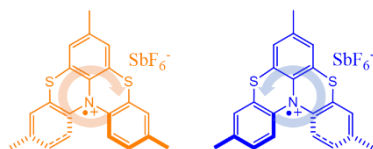


Fig. 9 Molecular structure of thia[4]helicene

Finally, continuous wave electron spin resonance (ESR) spectroscopy was exploited to investigate radical properties on bulk phase (both solution and single crystal) and then to get information about the interaction and the presence of spin 1/2 species in the nanostructured molecular monolayer. The results demonstrate that the monolayer is assembled avoiding any chemical modification and maintaining the paramagnetic character.

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Development of a combined methodology towards mechanistic investigation of sustainable light-activated catalysts

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Photocatalysis has been an important research field in the last 40 years and has become increasingly more common as an easy way to obtain unusual reactivity and greener synthetic pathways. While compounds of rare transition metals such as ruthenium and iridium are commonly employed,[1] in recent years the interest has started to shift towards different photocatalysts, such as metal-free organic dyes and compounds containing more easily available transition metals, such as copper, which not only allow for more economically affordable catalysts but also open up reactions and selectivity that were previously not accessible or unexplored.[2] In the frame of the the European Programme MSCA-Horizon 2020 "Paramagnetic Species in Catalysis Research (PARACAT)" we are working to shed light on synthetic pathways that employ these alternatives, such as the reaction of allyl-benzene and thiosulphonate to obtain aryl-thiols employing cromophore 9-mesityl-10-methylacridinium perchlorate or copper complexes. These synthetic protocols can use visible light and a green solvent resulting in high yield and minimal waste products.[3] EPR spectroscopic and fluorescence results will be presented and related to different mechanistic proposals.

We gratefully acknowledge funding from Marie Skłodowska-Curie Joint Doctorate grant agreement No 813209.

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^{17}O ENDOR detection of water molecules on the radical transfer pathway of ribonucleotide reductase

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Water plays an essential role in many biological reactions, which goes far beyond the function of simple solvent. Specifically its involvement in electron transfer mechanisms has been of great interest. The detection of individual water molecules can be achieved by high resolution x-ray diffraction, however crystallization of transient protein complexes limits the application of this method. Spectroscopy methods do not suffer from this limitation and electron-nuclear double resonance (ENDOR) spectroscopy is particularly well suited to detect water molecules in the vicinity of

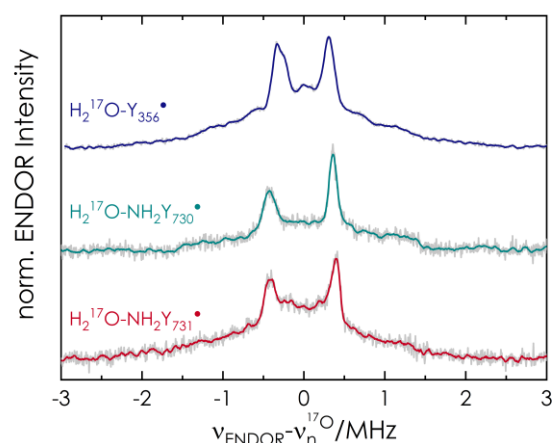


Figure 1. 94 GHz ^{17}O Mims ENDOR of radical intermediates $\text{Y}_{356}^{\bullet}$, $\text{NH}_2\text{Y}_{730}^{\bullet}$ and $\text{NH}_2\text{Y}_{731}^{\bullet}$ in *E. coli* RNR.

paramagnetic centres, such as radical intermediates in biological reactions. In contrast to the use of deuterium or proton ENDOR, where contributions from other exchangeable protons can always be present, ^{17}O ENDOR provides the specificity needed to unambiguously assign spectral signatures to water molecules. While ^{17}O ENDOR has been established as a method to detect water molecules at transition metal ions, it has thus far not been utilized to detect them around organic radical intermediates.¹⁻² Here, we present high-field (3.4 and 9.4 T) ^{17}O ENDOR experiments of three distinct radical intermediates in the active complex of *E. coli* ribonucleotide reductase. We confirm previous predictions³⁻⁴ and give the first direct experimental evidence of water molecules at these intermediates. We compare the experimental spectra with spectral simulations and small scale density-functional theory calculations to derive a binding structure of the water molecules around the radical intermediates.

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Studying conformational dynamics of the SLC gene family homologue GltTk using advanced magnetic resonance techniques

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The homotrimeric aspartate membrane transporter from *Thermococcus kodakarensis* (GltTk) is an archaeal homologue of the mammalian glutamate transporters belonging to the Solute Carrier 1 (SLC1) membrane transporter family, which also includes the excitatory amino acid transporters (EAAT's). Dysfunction of these systems leads to neurological disorders such as schizophrenia, Alzheimer's disease and epilepsy. GltTk has the primary role of regulating neurotransmitter levels in the synaptic cleft to prevent over-stimulation. Another SLC1 family member, GltPh, is often used as a model system for these transporters and is well studied, however, GltTk isn't currently well characterised with biophysical techniques. Here we aim to study the functional conformational changes and associated dynamics of GltTk using a range of (both NMR and EPR) magnetic resonance approaches. Cysteine variants have been designed, which upon spin labelling, are able to report on functionally relevant conformations using advanced EPR techniques, including distance determination methods (PELDOR) to identify key structural intermediates of the catalytic cycle. Further, we have employed Saturation-Transfer Difference (STD)-NMR methods to develop a novel approach to correlate the thermodynamic properties of substrate binding with conformational intermediates. A key step in this process is to determine whether data attained in detergent micelles reflects that obtained in physiologically more relevant proteoliposomes.

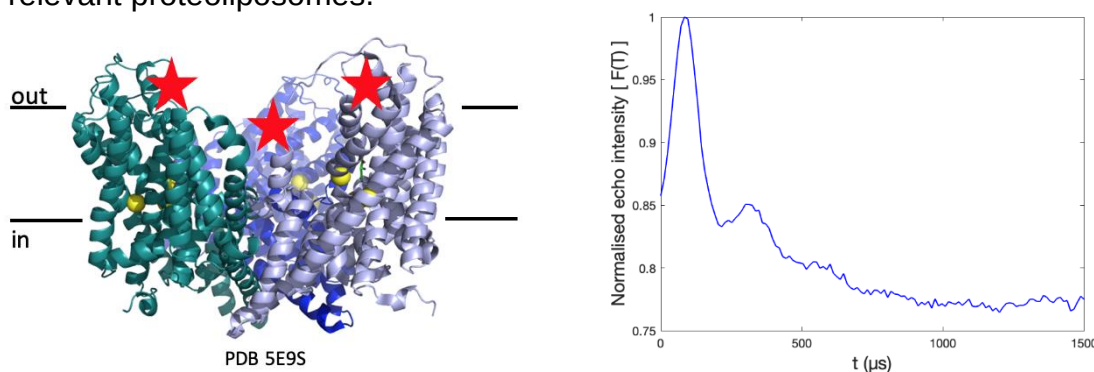


Figure 1 (left) A selected conformation of the dynamic homotrimeric protein GltTk (each protomer is shown in a different colour and transport-dependent sodium ions are also shown in yellow). The red stars represent one of the relative positions of the spin-labels attached to selected cysteine residues¹. (Right) PELDOR time trace of spin labelled GltTk (281C)².

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Co(II)-Based single-ion magnets with 1,1'-ferrocenediyl-bis(diphenylphosphine) metalloligands

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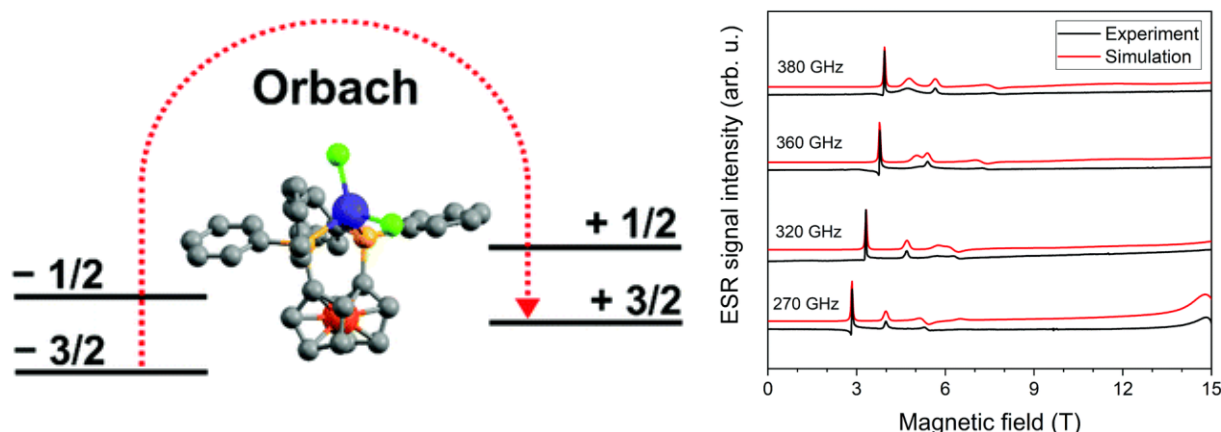
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Herein, we report on investigations of magnetic and spectroscopic properties of three heterobimetallic Fe(II)–Co(II) coordination compounds based on the tetracoordinate {CoP₂X₂} core encapsulated by dppf metalloligand, where X = Cl (**1**), Br (**2**), I (**3**), dppf = 1,1'-ferrocenediyl-bis(diphenylphosphine). The analysis of static magnetic data has revealed the presence of axial magnetic anisotropy in compounds (**1**) and (**2**) and this was further confirmed by high-frequency electron spin resonance (HF-ESR) spectroscopy. Dynamic magnetic data confirmed that (**1**) and (**2**) behave as field-induced Single-Ion Magnets (SIMs). Together with bulk studies, we have also tested the possibility of depositing (**2**) as thick films on Au(111), glass, and polymeric acetate by drop-casting as well as thermal sublimation, a key aspect for the development of future devices embedding these magnetic objects [1].



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High Frequency AWG Implementation at 94 GHz on HiPER

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We describe the implementation of a wideband arbitrary waveform generator (AWG) with very high spurious free dynamic range, which can fully exploit the 1 GHz bandwidth available from a kW pulsed spectrometer (HiPER) operating at 94 GHz.

The use of wideband AWGs has almost become standard in pulsed EPR. Shaped and frequency swept pulses can offer both better frequency selectivity and larger excitation bandwidths compared to rectangular pulses. However, in terms of sensitivity, it is arguably at the highest frequencies where they are poised to make the most impact, since most X- and Q-band spectrometers are already capable of exploiting most of their available bandwidth. Most implementations, at these lower frequencies, use analogue IQ mixers to modulate the main microwave transmission frequency directly. However, the performance of analogue IQ mixers degrades rapidly at higher frequencies, leading to inadequate suppression of the local oscillator (LO) and image frequencies. It is also possible to directly multiply a low frequency modulated waveform to a higher frequency, but this limits amplitude control and is susceptible to the phenomenon of spectral regrowth that introduces spurious frequencies. It is therefore better to use a direct up-conversion scheme.

We describe a system that takes advantage of the capabilities built into the two-channel M8190A 12-bit 12 GSa/s AWG from Keysight Technologies. This AWG can use an internal Direct Digital Synthesizer (DDS) to generate a high purity LO signal (in our case typically in the range 1300 to 2300 MHz) that is output from one channel and is used as the LO in a final down-conversion stage. A separate but completely coherent DDS provides the same digital LO that is internally modulated by a digital IQ mixer to provide the desired high purity modulated waveform on the other channel. This is then up-converted on to a 92.2 GHz LO signal, filtered and then amplified to provide the main transmission frequency over the required 93.5 to 94.5 GHz, at kW power levels. Control software allows a wide variety of waveforms, pulse sequences and phase cycling steps to be easily programmed.

The received signal is amplified and filtered before being coherently down-converted in two steps via the 92.2 GHz LO signal and the 1300 to 2300 MHz LO from the AWG, before the IQ signal outputs are digitised via a 2-channel fast sampling card.

The resulting waveforms have excellent dynamic range and are essentially free from spurious frequencies, and offer considerable flexibility in choice of excitation bandwidth and LO frequency. This set-up also simplifies the overall spectrometer design as other timing controls and the system clock are now derived only from the AWG. We provide a number of examples that illustrate the dual advantages of a spectrometer with high concentration sensitivity and GHz excitation bandwidths.

DeerLab and new aspects in dipolar EPR spectroscopy analysis

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The analysis of experimental data obtained from dipolar EPR spectroscopy techniques (DEER, RIDME, etc.) requires both accurate theoretical models of the underlying physics and robust numerical methods to estimate those model parameters that fit the experimental data.



DeerLab is a free, open-source software package for Python for data analysis of dipolar EPR spectroscopy [1]. It provides tools to implement arbitrary data analysis workflows, adapting to most needs. The program comes in the form of a scriptable toolbox accessible for all programming skills, enabling simple, flexible, and reproducible workflows.

We illustrate some of the new theoretical and methodological advancements included in DeerLab. These include:

- One-step analysis: fitting all model parameters (including non-parametric distance distributions) without the need for background correction or any pre-processing modifications of the signals.
- Uncertainty analysis: accurate and robust estimation of the uncertainty in results based on bootstrapping methods to calculate confidence intervals for any desired quantity.
- General global analysis: fitting any type and number of models to an arbitrary number of signals.
- Multi-pathway models: fully describing experiments such as 4-pulse, 5-pulse, or 7-pulse DEER with dipolar pathways or experiments such as RIDME or SIFTER in terms of harmonic pathways.
- Identifiability analysis: assessing whether the experimental data provide enough information to uniquely determine the best fit for a given model. If not, using new methodology to ensure the identifiability of the solutions.

For more information on features and installation of DeerLab, visit jeschkelab.github.io/DeerLab/index.html.

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Combining EPR spectroscopy with Circular Dichroism Spectroscopy to Investigate non-Covalent Interactions

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Non-covalent interactions are responsible for slight changes in the spectral properties of the systems investigated. We recently analysed the interaction of TEMPO, 4-carboxy-TEMPO and 4-amino-TEMPO with cyclodextrins at various pH values combining EPR spectroscopy with circular dichroism spectroscopy. The experimental data have been completed by computational analysis of preferred conformations of TEMPO radicals inside cyclodextrin cavities [1].

While the EPR data provide information regarding the orientation of the nitroxide group relative to the host cavity, and also on the strength of the complexation process, the circular dichroism data evidence the circular dichroism induced to the substituted TEMPO radicals as a result of complexation. The substituted TEMPO spin probes adopt the same preferential orientation within the cavity, irrespective of the cyclodextrin type, with the paramagnetic moiety included within the cavity for 4-carboxy TEMPO and exposed to the aqueous environment for 4-amino-TEMPO. The different localization of the paramagnetic moieties of the two probes accounts for the trends observed in the EPR spectrum, indicating a weaker interaction between 4-amino-TEMPO and cyclodextrins in terms of the polarity sensed by the probe and the molecular mobility of the unpaired electron. Moreover, the relative orientation of the electric transition moments of 4-amino-TEMPO and β -CD accounts for the weaker ICD signal observed experimentally.

These results prompted us to investigate the spectral properties of spin-labelled functionalised alginate in solutions and in corresponding gels by the same methods.

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Structural anomaly of glassy ionic liquids revealed by EPR

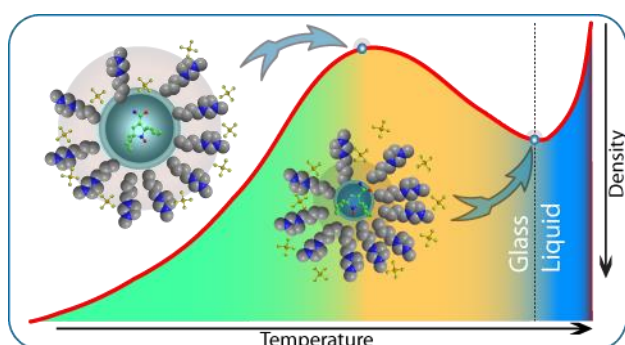
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Ionic liquids (ILs) show a variety of unusual and intriguing properties on a molecular level. In our group we discovered unprecedented suppression of molecular mobility near the glass transition (T_g), which is assigned to unusual structural rearrangements of glassy ILs on the nanometer scale [1-3]. In particular, the coexistence of two types of IL

environments was observed, one of which progressively suppresses the molecular mobility upon temperature increase between ($T_g - 60$ K) and T_g . This is a highly uncommon behavior, since most of known substances, including the same ILs in bulk, become less dense upon temperature increase, so it was termed “structural anomaly”. We used several independent electron paramagnetic resonance (EPR) approaches (continuous wave, pulse and time-resolved) that helpfully complement each other [4]. Recently, we implemented the developed complex EPR approach to investigate the influence of water content [5], IL cation alkyl chain length [6] and metal-organic frameworks embedding [7] on the structural anomaly in IL glasses and disclose its origins.

This work was supported by the Russian Science Foundation (No. 19-13-00071).

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SNR improvements in Pulsed EPR by applying Radar Signal Processing Techniques

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Coherent detection and phase cycling are standard methods in pulsed EPR to remove dc offsets, cancel gain and phase imbalances between the I and Q channels, maximise signal to noise, and discriminate between different coherence pathways.

However, most of these techniques assume that, or rely on, the relative phase remaining constant during an experiment. At low frequencies, for modern spectrometers, this is normally a very good approximation. However, at higher frequencies when larger superconducting magnets are necessary, it is often the case that pathways in the spectrometer get longer as the wavelength gets shorter. This means that temperature changes in the sample or the spectrometer can lead to significantly higher relative phase changes. Sensitivity to long term phase drifts can partially be ameliorated by detecting the absolute value from the IQ channels at the cost of $2^{1/2}$ in signal to noise, but small imbalances between the IQ channels can still remain troublesome in certain experiments, and limit sensitivity.

Most pulse spectrometers down-convert echo signals to baseband before sampling. However, there can be advantages to down-converting to a frequency well removed from dc (and the Nyquist frequency) and first manipulating the signal digitally in frequency space. In particular, it is now easy to remove dc offsets and IQ imbalances and other unwanted frequencies (before transforming back). This can help make small echo signals more apparent when optimising other experimental parameters. It also becomes possible to digitally correct for phase drift, or phase shifts introduced by the instrument, or experiment (such as the Bloch-Siegert shift). It can then also be helpful to apply matched filtering, either before or after digitally converting to baseband, particularly in experiments where the frequency is stepped and results coherently combined (in principle sometimes within T_1). Both coherent averaging and matched filtering can then lead to an increase in sensitivity. The gain from matched filtering is normally quite small for standard echoes but can be larger for echoes produced by composite pulses. Matched filtering also allows analogous techniques related to pulse compression methods commonly used in radar, which can be advantageous in certain circumstances.

In this poster we discuss such techniques and illustrate some of their advantages, particularly in the context of chirped pulses, composite pulses and frequency stepped experiments.

Hybrid Spintronic Materials from Conducting Polymers with Molecular Quantum Bits

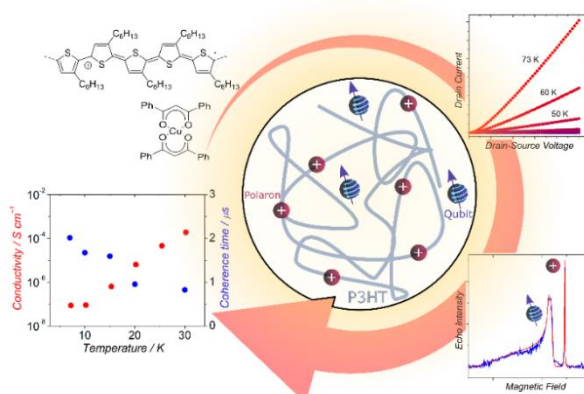
Michal Kern^{1,2}, Lorenzo Tesi², David Neusser³, Nadine Russegger¹, Mario Winkler¹, Alexander Allgaier¹, Yannic M. Gross³, Stefan Bechler⁴, Hannes S. Funk⁴, Li-Te Chang⁴, Jörg Schulze⁴, Sabine Ludwigs³ and Joris van Slageren¹

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Hybrid materials consisting of organic semiconductors and molecular quantum bits promise to provide a novel platform for quantum spintronic applications. However, investigations of such materials, elucidating both the electrical and quantum dynamical properties of the same material have never been reported. Here the preparation of hybrid materials consisting of conducting polymers and molecular quantum bits is reported. Organic field-effect transistor measurements demonstrate that the favorable electrical properties are preserved in the presence of the qubits. Chemical doping introduces charge carriers into the material, and variable-temperature charge transport measurements reveal the existence of mobile charge carriers at temperatures as low as 15 K. Importantly, quantum coherence of the qubit is shown to be preserved up to temperatures of at least 30 K, that is, in the presence of mobile charge carriers. These results pave the way for employing such hybrid materials in novel molecular quantum spintronic architectures. [1]

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Probing Structural Heterogeneities in Ionic Liquids using CW-EPR

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Ionic Liquids (ILs) possess a combination of properties which make them particularly interesting for a number of different applications, from catalysis to energy storage [1]. The majority of these properties arise from the fact that ILs exhibit a “medium-range ordering” and therefore, they combine characteristics from both molecular liquids and ionic salts [2]. This induces the existence of persistent local environments dominated by specific interaction types. To get insight into these environments, mostly theoretical [3] and spectroscopic [4] studies have been considered. The used methods focused specifically on investigating either neat ILs or ILs with very low concentration of solutes. However, for commercial applications, the effect of more concentrated solutions on the local environment should be considered. EPR characterization of nitroxide radicals, used as simple paramagnetic spies, introduced into these concentrated environments could be used to this end and present the aim of this work.

Here we study two alkyl-imidazolium bis(trifluoromethylsulfonyl)imide ILs with varying cation side alkyl-chains, with 2 and 8 carbons. This allows us to tune the polarity of the ILs and the size of the heterogeneous regions. We also investigate the effect of increasing the concentration of the different analogues of the TEMPO radical, in order to reveal interactions hidden at lower concentrations. Our results indicate that the microenvironments in the ILs cause high local radical concentrations, resulting in the observation of unusual exchange phenomena that require detailed investigation.

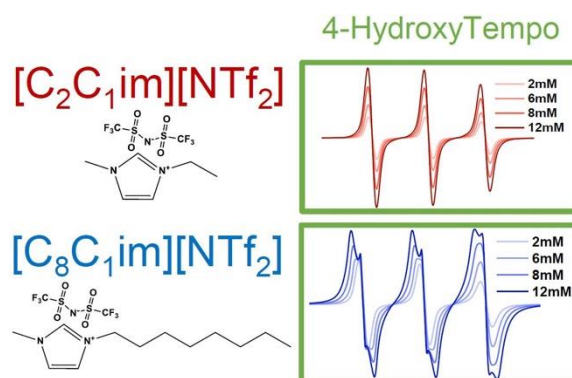


Figure 1. EPR spectra of 4-HydroxyTempo in 2 ILs at different concentrations.

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Application of EPR to Porphyrin-Protein Agents for Photodynamic Therapy

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Recently, a new type of spin labels based on photoexcited triplet molecules was proposed for nanometer scale distance measurements by pulsed dipolar electron paramagnetic resonance (PD EPR). However, such molecules are also actively used within biological complexes as photosensitizers for photodynamic therapy (PDT) of cancer. Up to date, the idea of using the photoexcited triplets simultaneously as PDT agents and as spin labels for PD EPR has never been employed.

In this work, we demonstrate that PD EPR in conjunction with other methods provides valuable information on the structure and function of PDT candidate complexes, exemplified here with porphyrins bound to human serum albumin (HSA). Distinct photosensitizers(PS) with different properties were used: several water soluble cationic porphyrins, amphiphilic mesotetrakis(4-hydroxyphenyl)porphyrin, chlorin e6 and pheophorbide a. HSA was singly nitroxide-labeled to provide a second tag for PD EPR measurements. Structural data of PD EPR were supported by other EPR techniques. We also studied the ability of the PS/HSA complexes to generate ¹O₂ and induce protein photocleavage, and thus established correlations between the location of binding sites of the protein and photoactivity of the bound PS. Therefore, pulsed EPR on complexes of proteins with photoexcited triplets is a promising approach for gaining structural and functional insights into such PDT agents.

This work was supported by Russian Science Foundation (no. 20-73-10239).

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The Use of NcAA and a Photoactivatable Nitroxide for Spin Labeling of Proteins with Potential for *in vivo* Applications

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EPR spectroscopy of diamagnetic bio-macromolecules is based on site-directed spin labeling (SDSL). In proteins, the post-translational conjugation of genetically encoded non-canonical amino acids (ncAA) with spin-labels allows for bioorthogonal reaction schemes. However, the potential for nitroxide labelling is underexplored. We report spin labelling *via* Diels-Alder inv. with a tailored **Photoactivatable Nitroxide for DA**inv reaction (PaNDA spin label).¹ In biological, i.e. reducing conditions, hereby the nitroxide moiety is shielded by a photoremovable protecting group with an attached tetra(ethylene glycol) unit to achieve water solubility. Our strategy features high reaction rates combined with high selectivity, and the possibility to control the paramagnetic potential of the nitroxide temporally.

Supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant Agreement number: 772027 – SPICE – ERC-2017-COG) and by the Deutsche Forschungsgemeinschaft (SFB 969, Project B5 and C3).

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Probing mixed duplex/quadruplex DNA structures via Cu^{II}-labeling

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G-quadruplexes (GQs) are DNA secondary structures formed by self-assembly of guanine-rich sequences via Hoogsteen base pairing and stabilized by central cations. *In vivo* formation of GQs in oncogene regulatory regions and within telomeres makes them an interesting target for cancer research¹. Various GQ species are known to assemble higher-order structures, which are believed to affect their biological activity. Additionally, oligonucleotides adopting mixed duplex/quadruplex conformations have recently gained a lot of attention². Thus, understanding these higher-order DNA structures and their formation is an important goal, towards which pulse dipolar EPR spectroscopy can make a substantial contribution.

Recently, we used square planar Cu^{II}(pyridine)₄ complexes covalently incorporated into tetramolecular GQs as spin labels to gain insight into the GQ dimerization via π -stacking of terminal G-tetrads.³ In the present work we extend the EPR-based approach to novel DNA structures representing two unimolecular GQs connected via a duplex bridge (Fig. A). The structures are formed by two oligonucleotides,

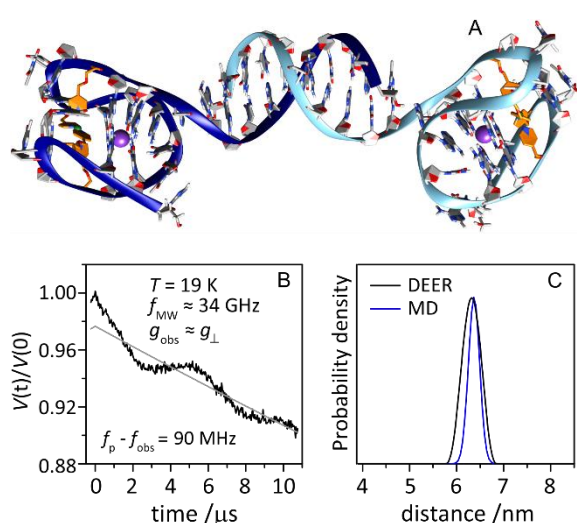


Figure. (A) MD-derived model of two duplex-bridged spin-labeled GQs; (B) DEER trace with background; (C) DeerAnalysis-derived Cu-Cu distance distribution with the MD result.

synthesized by solid-phase DNA synthesis, each containing the same GQ-forming sequence with pyridine-modified nucleotides capable of binding Cu^{II}. Additional, complementary single-stranded overhangs are attached to the 3' ends.

Such a design allowed the linking of two spin-labeled unimolecular GQs by a duplex bridge, as evidenced by DEER (Fig. B,C). The clear dipolar modulation yielded a mean Cu-Cu distance of 6.3 nm, in excellent agreement with the MD simulations. Our results demonstrate that the Cu^{II}(pyridine)₄ spin labels can be successfully applied to complicated DNA structures, containing biologically relevant duplex/quadruplex junctions.

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Chromium Environment in Cr-doped SAPO-5 from Spin Density Study

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In this poster we present EPR investigations accompanied by DFT modelling on the local environment of Cr in the Cr-doped SAPO-5 molecular sieve. The X-band (9.5 GHz) continuous wave (cw) and Q-band (34 GHz) electron spin echo (ESE) detected EPR spectra showed the signal of Cr(V) species after calcination. This treatment reported in the work of Zhu and Kevan suggested incorporation of the Cr(V) ions at the P(V) sites.¹ In this work, the hyperfine sublevel correlation (HYSCORE) spectroscopy was employed in conjunction with DFT modelling to determine the location of the Cr(V) ions in the material. The interaction of the unpaired electron of the Cr(V) ions with the ²⁷Al could be resolved and allowing detailed analysis of the local environment around the Cr(V). The interpretation from the experimental results corroborated with the DFT modelling is found consistent with the isolated Cr(V) species isomorphously substitute the framework P(V).

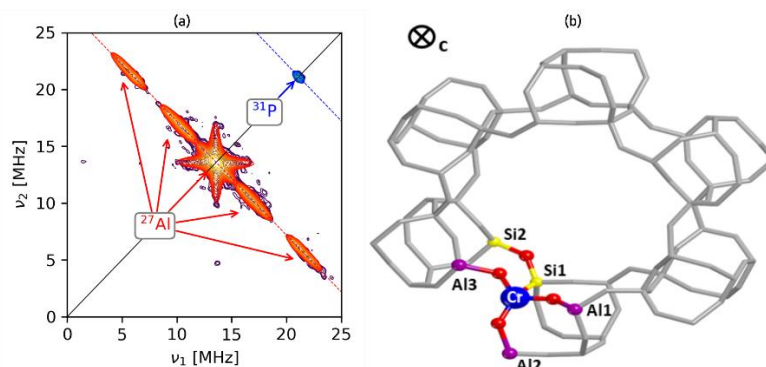


Figure1. (a) Experimental and simulated Q-band HYSCORE spectrum of the Cr(V) species in the SAPO-5. (b) Optimized structure of CrSAPO-5 in periodic modelling.

Acknowledgement: This work is part of the PARACAT project that received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813209

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Design and Applications of Dual Mode Microwave Resonators in Electro Paramagnetic Resonance Spectroscopy

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Previously we have demonstrated the design and functionality of a novel dual-mode X-band EPR resonator, where two cavity modes are simultaneously employed, at ca. 9.5 GHz frequency (TM₁₁₀) for EPR detection and at ca. 6.1 GHz frequency (TM₀₁₀) for sample perturbation via dielectric heating.^[1] In the first generation dual-mode resonator, the EPR port and heating port were located 90° to one another which limited the sample size to a 1.8 mm quartz tube; in this configuration, critical coupling of the resonator proved difficult.

A second generation dual-mode cavity was therefore developed, whereby the heating port has been positioned 135° from the EPR inlet port such that a standard 4 mm quartz tube can be utilized; this position additionally provides easier coupling. Through the design and testing of this new resonator, we have come to understand the importance of port positioning, and particularly the pros and cons between the two designs aspects of these novel dual-mode resonators. Both resonator designs have proved effective in dielectric heating, as demonstrated using a standard Cu(acac)₂ complex via the line shape analysis and rotational correlation times (τ_R).

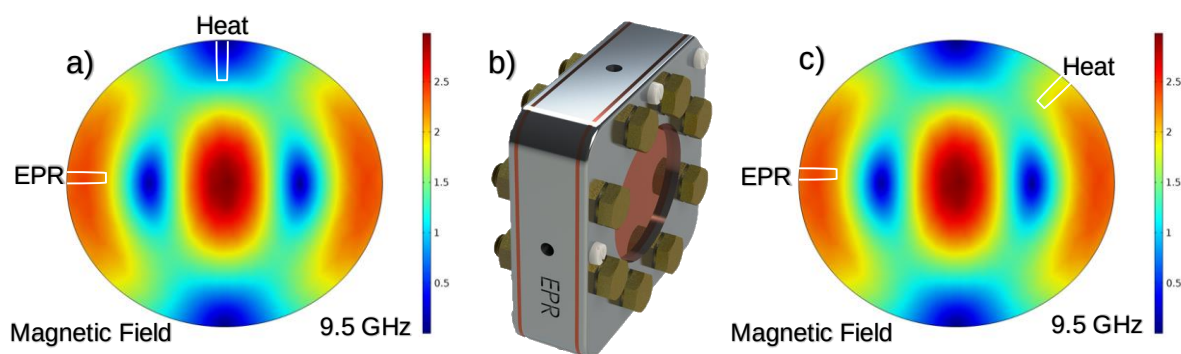


Figure 10: a) Port placement for the 1st generation dual-mode cavity, b) render design of 2nd generation dual-mode cavity and c) port placement of the 2nd generation dual-mode cavity.

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Theoretical and spectroscopic study of Cu(II) binding in flavonoids

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Flavonoids are one of the largest groups of polyphenolic compounds present in plants, possessing significant antioxidant and prooxidant activities [1]. It has been shown that myricetin, morin, taxifolin and 3',4'-dihydroxyflavone are able to form stable complexes with Cu(II) ion, capable of ROS scavenging via Fenton reaction [2]. The Cu(II) binding mode in this set of flavonoids (see Figure 1) is inspected using DFT theory and QTAIM method [3]. The results of DFT calculations are used to help with interpretation of experimental EPR and UV-Vis spectra [4].

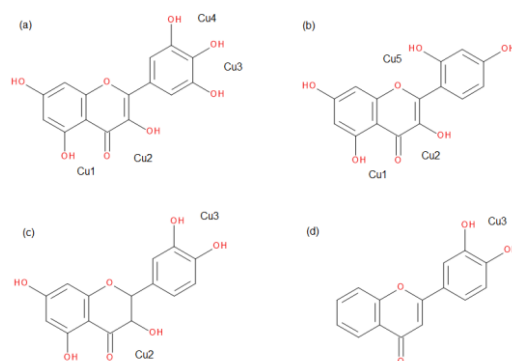


Figure 1. Scheme of the studied flavonoids with potential Cu(II) acceptor sites

We are grateful to the Slovak Grant Agencies APVV (contract No. APVV-15-0079 and APVV-19-0087), VEGA (contracts No. 1/0139/20 and 1/0482/20) and SIVVP project(ITMS code 26230120002).

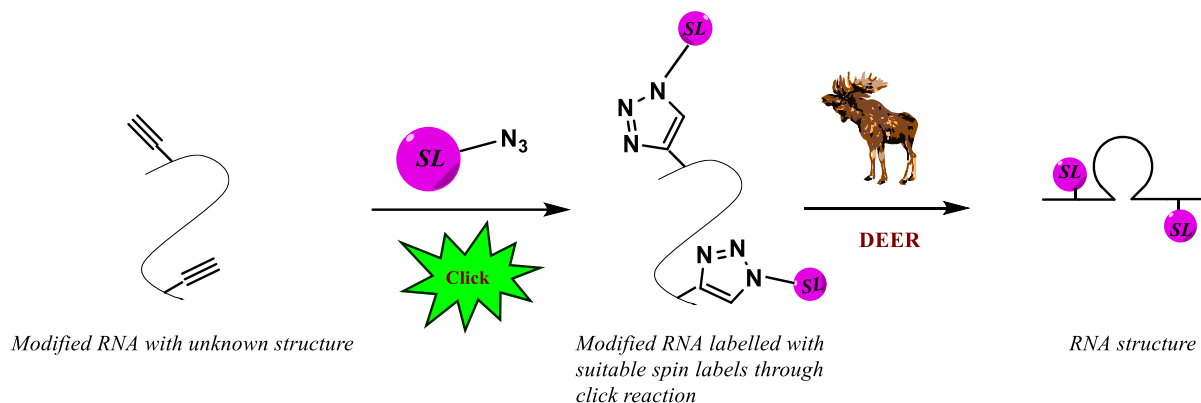
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 - [3] M. Šimunková, M. Valko, L. Bučinský, M. Malček, *J. Mol. Struct.*, 2020, **1222**, 128923.
 - [4] M. Šimunková, M. Malček, *Acta Chim. Slov.*, 2020, **13**, 1-11.

Progress towards click spin labelling RNA in a base independent fashion

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RNA is a polymeric molecule involved in many biological processes, it can assume a wide range of conformations and it interacts with different proteins and co-factors. As little is known about RNA secondary and tertiary structures, investigating the correlation between their conformation and their function is of great interest. My research is focussed on the application of to study the structure of long non-coding genomic RNA. Since EPR can only be applied to molecules that are paramagnetic, it is necessary to label the RNA with suitable spin labels¹. We are investigating the use of Cu(I)-catalysed azide-alkyne cycloaddition (CuAAC or “Click”) reaction previously shown in DNA^{2,3}. This requires two reactant species: an alkyne and an azide. Therefore the aim is to synthesize spin labels and nucleotides suitably modified with these functional groups to allow spin labelling via the Click reaction.



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Spin-Correlated Radical Pairs in Avian Cryptochromes

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Cryptochromes are photoreceptor proteins that occur in all kingdoms of life. As well as their role in circadian rhythm (the natural process regulating sleep cycles), these proteins are believed to be vital in the migratory sense of certain night-migratory songbirds.

Excitation of cryptochromes with blue light initiates an electron transfer cascade; the electron acceptor is a flavin cofactor found within the protein, while the ultimate donor is a tryptophan residue. The resulting radical pair is spin-correlated, as the singlet state precursor is not an eigenstate of the total spin Hamiltonian. The coherent evolution of the system (involving interconversion between singlet and triplet states) is field-dependent and considered to be the source of magnetoreception in many species.

Cryptochromes are being studied using a wide variety of optical and EPR-based methods. Analysis via EPR is of particular interest as it (a) yields structural information about the radical pair, such as the distance between the two spin centres, via the dipolar coupling, and (b) allows characterisation of the hyperfine couplings which drive the magnetosensitivity of the radical pair in the fields experienced by the bird. The principal methods used in this work are time-resolved EPR (TREPR) and out-of-phase electron spin echo envelope modulation (ESEEM).

The TREPR spectra of spin-correlated radical pairs could not be simulated by any existing software packages. A model that reflects the many parameters present in the system has since been constructed, allowing analysis of factors such as the many electron-nuclear hyperfine couplings as well as the interactions between electron spins.

The inter-electron spin couplings are also determined with high accuracy in out-of-phase ESEEM. Knowledge of the so-obtained dipolar coupling, and thus the distance between radicals, yields information on the identity of the radical pair [1].

Here we report an EPR study on cryptochromes from a variety of organisms and elucidate the effects of parameters such as temperature and point mutation on the characteristics of the magnetosensitive radical pairs.

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Multifrequency EPR investigation on isolated Ti(III) Species on the Surface of Pre-active Ziegler Natta Catalysts

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2) *University of Antwerp, Department of Chemistry, Universiteitsplein 1, 2610 Antwerp, Belgium.*

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A combination of X-, Q- and W-band CW and pulse EPR spectroscopy have been used to study the nature of Ti(III) species, introduced in working models of industrial Ziegler Natta catalyst precursors, consisting of $\text{MgCl}_2/\text{TiCl}_4$ binary systems, with and without Lewis bases. In Ziegler Natta catalysts, Ti(III) plays the double role of active catalytic species and unconventional spin probe. On the binary system, two dominant Ti(III) species, characterized by distinctively different EPR spectra, are observed. $^{35,37}\text{Cl}$ Q-Band HYSCORE spectra allow estimating the hyperfine and nuclear quadrupole interactions of the directly coordinated Cl. A hyperfine dipolar contribution of the order of 5 MHz and nuclear quadrupole interaction of the order of $e^2qQ/h = 9$ MHz is found. Interestingly, the two dominant EPR-active species are selectively suppressed by the presence of different Lewis bases, indicating the possibility to address the long-standing issue of the influence of Lewis bases in driving specific morphological configurations and influencing the catalytic properties of Ti(III) active sites.

Acknowledgements This work is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement no. 813209

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In-situ EPR study of structural transitions of the Metal-Organic Framework DUT-49(Cu) upon physi- and chemisorption

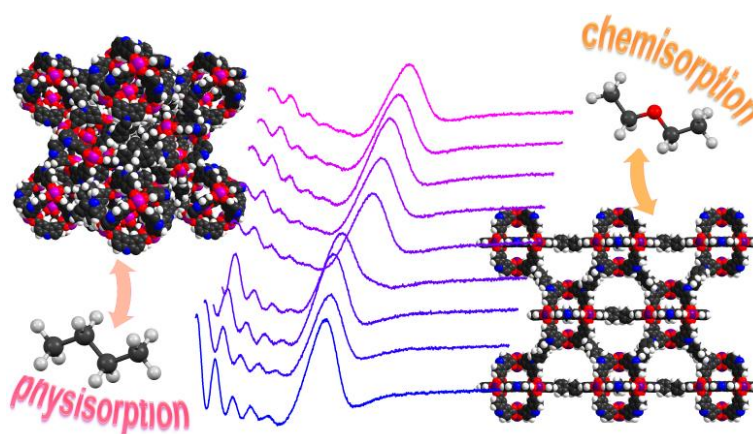
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Flexible metal-organic frameworks (MOFs) exhibit a variety of phenomena attractive for basic and applied science. DUT-49(Cu) is one of the remarkable representatives of such MOFs, where phase transitions are coupled to pressure amplification and “negative gas adsorption” [1]. In this work we report important insights into structural transitions of DUT-49(Cu) upon physi- and chemisorption of gases and volatile liquids obtained by *in situ* Electron Paramagnetic Resonance (EPR) spectroscopy [2]. In this method, phase transitions are detected via the zero-field splitting in dimeric copper(II) units. First, new approach was validated upon physisorption of *n*-butane. Then, using diethyl ether, we for the first time demonstrated that chemisorption can also trigger phase transition in DUT-49(Cu). Based on the EPR results, the transition and coordination appear completely reversible. The developed EPR-based approach can also be extended to other flexible MOFs containing paramagnetic metal paddle-wheels, where high sensitivity and spectral resolution allow *in situ* studies of stimuli-induced structural variability.

Acknowledgements: The reported study was funded by RFBR according to the research project № 18-29-04013



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Study of ZIF-8 pressure-induced amorphization by spin probe approach

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Electron paramagnetic resonance (EPR) is a spectroscopic technique for studying systems having unpaired electrons. The method is being successfully applied in many areas of science, including metal-organic frameworks (MOFs). For instance, EPR spectroscopy enabled investigation of photocatalysis in MOFs occurring due to electron transfer inside the framework, structural transitions driven by temperature or pressure in flexible MOFs using spin probe detection, determination of parameters relevant for quantum computing, and magnetic properties of these systems. However, despite the extensive range of applications, EPR has not yet become a regular tool for studying MOFs, partly because of the difficulties arising during preparation of samples with EPR-active species in the structure. Previously we have developed approach for incorporation of the nitroxyl radical in ZIF-8 cavity [1]. Stable radical TEMPO encapsulated in ZIF-8 was demonstrated to be an excellent probe to study pore permeability by various solvents.[1] Known that spin probes in MOFs can also allow obtaining important information on different structural rearrangements of the framework induced by external stimuli.

Pressure-induced amorphization is one of the processes inhibiting functional properties of MOFs. Such amorphization often occurs when MOFs are being shaped for practical applications, as well as during certain exploitations. Typically, the porosity of MOFs, which is crucial for sorption, separation, and catalysis, suffers under external pressure. We report a new experimental approach for efficient monitoring of pressure-induced processes in MOFs that employs trace amounts of spin probes (stable nitroxide radicals) embedded in the pores of MOF and detection by electron paramagnetic resonance. EPR spectra of spin probes in MOF ZIF-8 demonstrate significant changes upon pressure-induced amorphization, whose extent can be quantitatively determined from the spectral shapes. Moreover, stabilization of ZIF-8 against amorphization via reversible adsorption of various guests was studied using this approach. Mitigation effect depends on diffusion parameters and localization of guest molecules in the cavity, and maintaining of the structure and permeability up to 80% was achieved even at 1.15 GPa applied. Therefore, the proposed methodology allows significant mitigation of MOF amorphization under external pressure and conveys further perspectives of the controlled adjustment of stabilizing agents for various MOFs and their applications.

Acknowledgements: The reported study was funded by RFBR and Novosibirsk region according to the research project № 19-43-543030.

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Spin Delocalisation in Porphyrin Systems

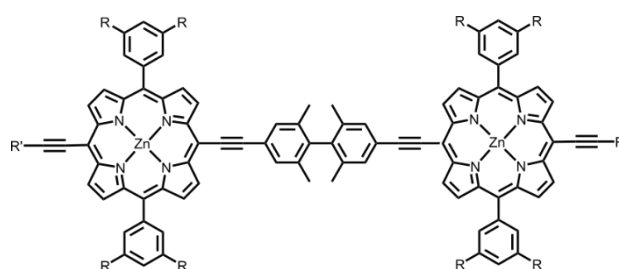
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Covalently linked multi-porphyrin systems have found applications in a range of contemporary research fields, such as molecular electronics, organic spintronics and semiconductors [1—2].

The electron distributions in the paramagnetic states (both ionic doublet and photoexcited triplet states) of linear biphenyl-linked Zn porphyrin oligomers are investigated by continuous wave and pulse EPR methods [3—5]. The spin delocalisation is effectively probed via the hyperfine couplings with ENDOR and ESSEM techniques and the zero-field splitting, in the case of triplet states, using transient continuous wave EPR. Measurements performed over a temperature range will provide additional information into the electron delocalisation pattern. For the radical cation state, the proton and nitrogen hyperfine interactions, observed in frozen solution, indicate the bridging unit prevents complete delocalisation within a dimer system. The experimental data are interpreted in the context of DFT geometry optimisation and EPR parameter calculations.



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An advanced EPR study to explore the Cu^{II}- TREN complexes with trigonal bipyramidal structure

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The oxidation of alcohols to aldehydes, ketones and carboxylic acids is probably the most widely used category of oxidation reaction in organic chemistry. For years, the platinum group metals (PGMs) were the centre of investigations for the selective oxidation of alcohols. However, PGMs are not sustainable [1]. In nature, the fungal copper enzyme galactose oxidase (GAO) converts primary alcohols to aldehydes. Since the use of copper as a base metal is much more sustainable, a lot of effort has been put into the use of copper complexes, mimicking this enzymatic centre for different catalytic oxidation reactions in organic chemistry [2]. Homogeneous Cu/nitroxyl- radical catalysts have been introduced almost 50 years ago for the aerobic alcohol oxidation when Brackman and Gasbeek first reported the oxidation of methanol with a (phenanthroline) Cu^{II}/di-tert-butyl nitroxyl cocatalyst system [3]. Herein this project, Cu^{II}-complexes with a tripodal ligand named Tris(2-aminoethyl)amine (Tren) coordinated to the metal centre have been studied due to the ability of the multidentate ligands to control the redox activity of the Cu^{II} centres. The geometry and electronic structure of the Cu^{II} complexes were investigated using a series of advanced EPR techniques like high frequency and pulse EPR. The studies have been performed in different ligand-to-metal ratios and at different pH values.

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Copl, a novel periplasmic protein involved in bacterial copper resistance.

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Copl is a periplasmic protein of 15kDa which is induced with high copper concentration and is directly involved in the copper resistance of the purple bacterium, *Rubrivivax gelatinosus*. [1] So far the 3D structure and the copper resistance mechanism are unknown. EPR studies we have performed show that there are two specific Cu(II) binding sites: a green cupredoxin T1.5 site conferring its colour to the protein, and a square planar (T2) site located in the N-terminal region. The latter site is not well conserved among Copl analogs and not required for copper resistance. On the other hand, the green cupredoxin site, for which only few examples are known in the literature, is fully conserved and mandatory. To get insight into the mechanism of this novel protein, we are first performing a combined EPR and NMR study to better characterize these sites structurally. The results we have obtained so far will be presented and discussed in the context of related copper proteins.

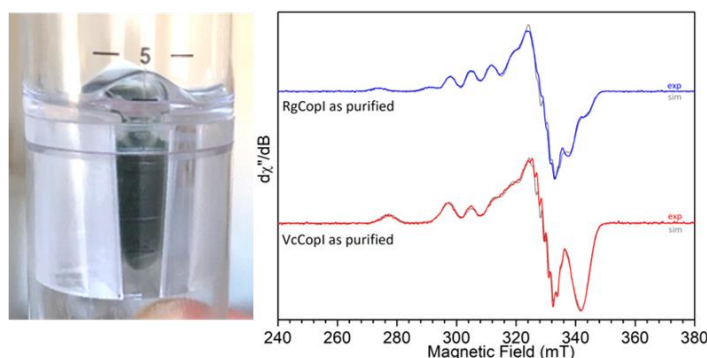


Figure 1. Left : purified soluble fraction containing Copl. Right : EPR spectrum of Copl from *R. gelatinosus* (blue) and Copl from *V. cholerae* (red).

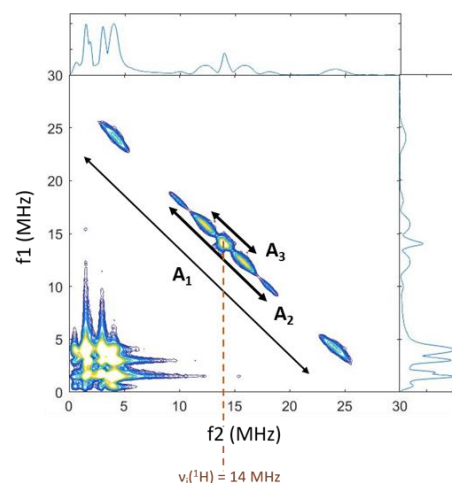


Figure 2. 6-pulse HYSCORE spectrum of the green cupredoxin site.

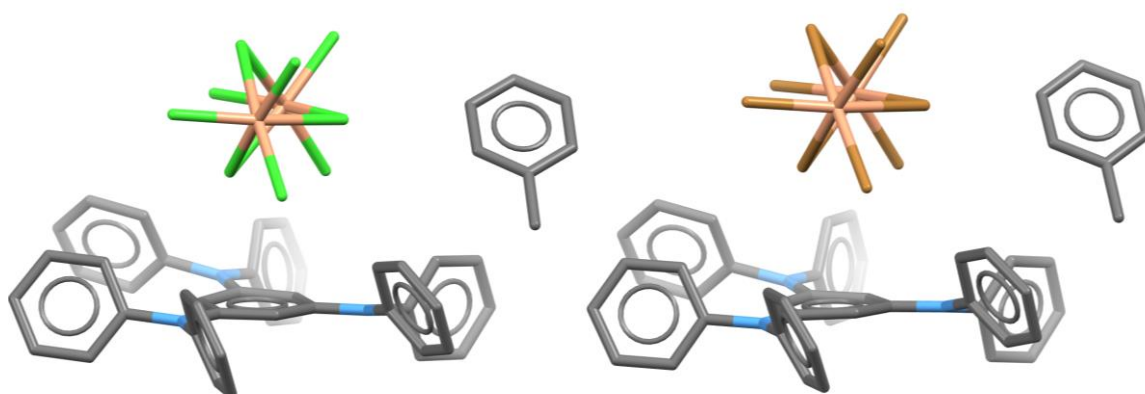
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The Synthesis, Rearrangement, Crystallization and EPR Spectroscopy of Tertiary Amine Radical Cations

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High-valent metal halides have been used to perform one-electron oxidation on neutral tertiary amines, to generate and crystallise the corresponding amine radical cations in a one-step, one-pot method. In crystalline form, the radical cation is counterbalanced by a complex anion of the metal halide in unchanged oxidation state. In EPR spectra performed in a coordinating solvent, the metal halide is shown to have undergone one-electron reduction. In certain cases, further reaction of a tertiary amine radical to give a bis(amino) compound through dimerization/rearrangement is observed, leading to a new radical pathway for the synthesis of tertiary bis-amines. Of particular interest is the rearrangement/dimerization of neutral tris(4-bromophenyl)amine, which successfully produces the radical cation of a bis(amine) believed to be contained in the decomposition product of Magic Blue¹.



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Spin-spin interactions in nitronyl nitroxyl mono- and biradicals studied by X-band EPR spectroscopy

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Organic mono- and biradicals are building blocks for obtaining molecular magnetic materials exhibiting useful physical properties or functions. These objects show promise for applications in spintronics as well as bistable memory devices and sensing materials [1].

Intra and intermolecular electron spin-spin interaction determines the macroscopic magnetic properties of paramagnetic substances based on mono- and biradicals [2]. The general nature of the exchange interaction in the substance under study can be characterized by the SQUID magnetometry. In turn, the electron paramagnetic resonance (EPR) spectroscopy makes it possible to determine the g-tensor of the spin system, the amplitude of the dipole-dipole interaction, and estimate the amplitude of the spin-spin exchange interaction.

In this work the EPR was used to study the intermolecular spin-spin exchange interaction in the crystal of 2-(5-methyl-1H-imidazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl monoradical. The sign and amplitude of the intramolecular exchange interaction in 1,1,2,3,3-pentamethylenepropane biradical with two nitronyl nitroxides (DR1) [2] was also determined in crystal and in solution. The parameters of the dipole-dipole interaction were determined, and the longitudinal and transverse spin relaxation times of the triplet state were measured by pulsed EPR spectroscopy for the dissolved biradical DR1. The obtained results are important for understanding the effect of exchange interactions on the spin relaxation processes in such systems.

We are grateful to Dr. S.E. Tolstikov, Dr. E.Yu. Fursova and Prof. V.I. Ovcharenko for the samples provided.

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Interdimeric Couplings and Spin Entanglement in Copper Acetate

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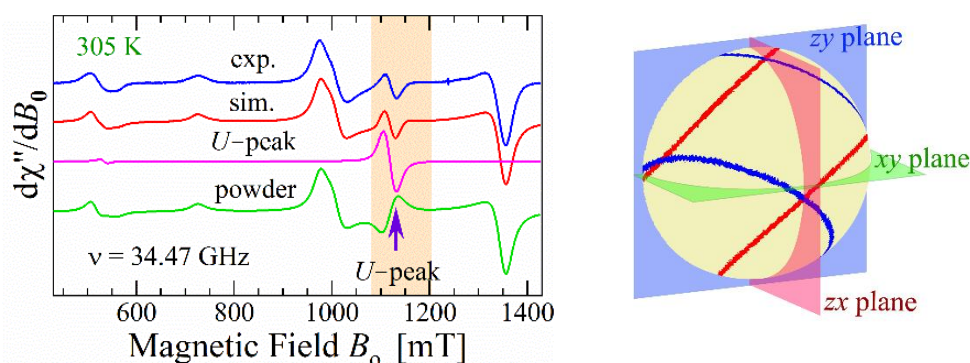
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Dimeric compounds having molecular units with pairs of spins $\mathbf{S}_1$ and $\mathbf{S}_2$ connected by intradimeric exchange coupling J_0 ($H_0 = -J_0 \mathbf{S}_1 \cdot \mathbf{S}_2$), and magnetically isolated in a crystal lattice, are non-trivial quantum spin systems, having primary roles in magnetism. Copper acetate monohydrate, $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$, here called CAH, has been investigated over the years and provided important information about superexchange couplings and magnetic behaviour. However, we have not found studies on the interdimeric couplings J' in CAH. They introduce spin entanglement and a spin dynamics having a prominent role in the behaviour of molecular magnets. We report a multifrequency Electron Paramagnetic Resonance (EPR) study of CAH in a wide range of T in single-crystal and powder samples explaining spectral features arising from weak interdimeric couplings ($|J'/J_0| \sim 10^{-5}$). When the two absorption peaks $m_s = -1 \leftrightarrow 0$ and $m_s = +1 \leftrightarrow 0$ in single-crystal spectra cross at the magic angles, they merge and narrow modulated by J' . As a consequence, powder spectra exhibit an additional feature named U-peak [1,2] shown in the spectra of the figure, collecting the absorptions coming from spins oriented within the “magic rings” (locus of magic angles) indicated in red circles (dimeric site A) and blue circles (dimeric site B) in the sphere of the figure. The orientations contained in the magic rings give rise to an entangled phase, which may be tuned with the orientation of an external magnetic field $\mathbf{B}_0$. Other orientations give rise to the standard dimeric spectrum. We propose a model for the interdimeric coupling effects, based on the crystal structure and the chemical paths for superexchange, analysing and modelling features of the observed EPR spectra considering these effects with results that contribute to a better description of the role of this coupling in the magnetic phases.



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Film Electrochemistry coupled to EPR Spectroscopy: Methodology and Applications

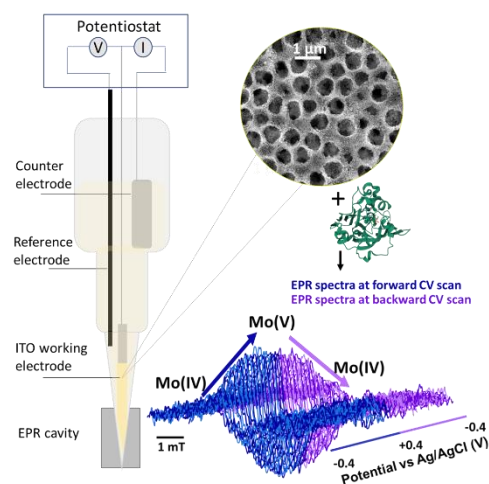
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The combination of electron paramagnetic resonance (EPR) spectroscopy with film electrochemistry (FE) provides a novel and powerful platform for the study of redox-active species, including large metalloproteins. The development of an accurate, robust and user-friendly FE-EPR system allows wide application of these combined techniques for the detection of paramagnetic species, including buried redox centres in proteins, with direct potential control [1], thus opening up the possibility for new mechanistic insights into redox-based processes in complex molecules irrespective of their size. However, technical challenges such as current response, robustness and controlling conductivity still need to be overcome to enable the application of FE-EPR to (bio)catalytic processes.

Here, we demonstrate simultaneous film electrochemical and EPR measurements *in situ* and *in flow*. The new working electrodes consist of easy-to-make and robust 2D indium-tin-oxide (ITO) electrodes and exhibit a quasi-instantaneous current response. Moreover, the 2D design permits the construction of tuneable inverse opal structures of ITO, paving the way for applications to large membrane proteins [2]. Nitroxide radicals and soluble proteins are used as proof of concept and applications to more complex membrane systems are underway.



PFE-EPR setup and application on molybdenum protein.

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Arresting the Catalytic Arginine in Chlorite Dismutases: Impact on Heme Coordination, Thermal Stability, and Catalysis

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Chlorite dismutases (Clds) are heme *b*-containing oxidoreductases which possess the unique ability to decompose chlorite (ClO_2^-), often found as an environmental pollutant, into harmless Cl^- and O_2 . Their investigation thus opens ways for potential biotechnological and bioremediation applications [1]. In our recently published work [2] we focus on the dynamics of the fully conserved arginine which sits at the distal site of the heme moiety. Indeed, this residue has been proposed to switch between two conformations during Clds turnover, even though its exact role in the catalytic cycle still needs to be elucidated. To understand the impact of the flexibility of this amino acid on iron coordination, structure and catalysis, Cld from *Cyanothece* sp. PCC7425 (CCld) was used as a model system. In particular, to modulate the conformational dynamics of the arginine, two mutants of CCld were generated, where a conserved glutamine (Q74), normally hydrogen-bonded to the arginine in the wild-type form, is exchanged either with valine (Q74V) or glutamic acid (Q74E). Here, an insight on the electronic configuration of ferric wild-type CCld and its variants is presented. The results obtained by CW EPR spectroscopy are discussed with respect to pH and active site architecture, to provide a detailed analysis of the altered hydrogen-bonding network of the distal catalytic arginine. This work was carried out in the frame of the PARACAT project (Paramagnetic Species in Catalysis Research), which received funding from the European Union's Horizon 2020 research and innovation program under Marie Skłodowska-Curie Grant Agreement n° 813209.

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Kaempferol: Protective Role in Cu Fenton Reaction monitored by EPR Spin Trapping

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The beneficial effects of flavonoids have been associated with their ability to prevent oxidative damage to living organisms. Metal ions coordinated by flavonoids usually exhibit a suppressed catalytic activity in the Fenton reaction and thus a suppressed formation of ROS. [1] The protective role of flavonoid kaempferol in a copper-catalysed

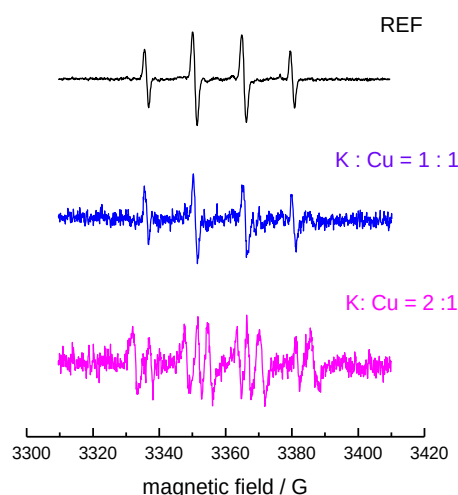


Fig. 1 Experimental EPR spectra obtained in the system $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{DMPO}/\text{DMSO}-\text{H}_2\text{O}$ (1:4; v:v), reference vs. addition of kaempferol.

Fenton reaction system was studied with the help of DMPO spin trap. The observation of DMPO- $\text{OH}^\bullet$ spin adducts is reflecting the efficient generation of hydroxyl radicals in the system. [2] Series of experiments was conducted with spin-trapping agent BMPO. Also in this case the dominant generation of $\text{OH}^\bullet$ adducts was observed. The addition of kaempferol to the reference system led to a significant decrease in the EPR signal intensity as is shown in Figure 1. In addition to DMPO- $\text{OH}^\bullet$ spin adducts, based on a simulation analysis signals were attributed to superoxide radical anions, detected as the $\text{DMPO-O}_2^\bullet$ spin adduct, and methyl radicals, detected as the DMPO-CH_3 spin adduct. The results demonstrated that coordination of kaempferol to Cu(II) ions results in a suppressed formation of hydroxyl radicals by 80%. This can be explained by a diminished catalytic activity of Cu(II) due to it being coordinated to the flavonoid.

This work was supported by Grants VEGA Project 1/0482/20 and APVV-19-008, STU Grants for Team of Young Researchers - CUSPK.

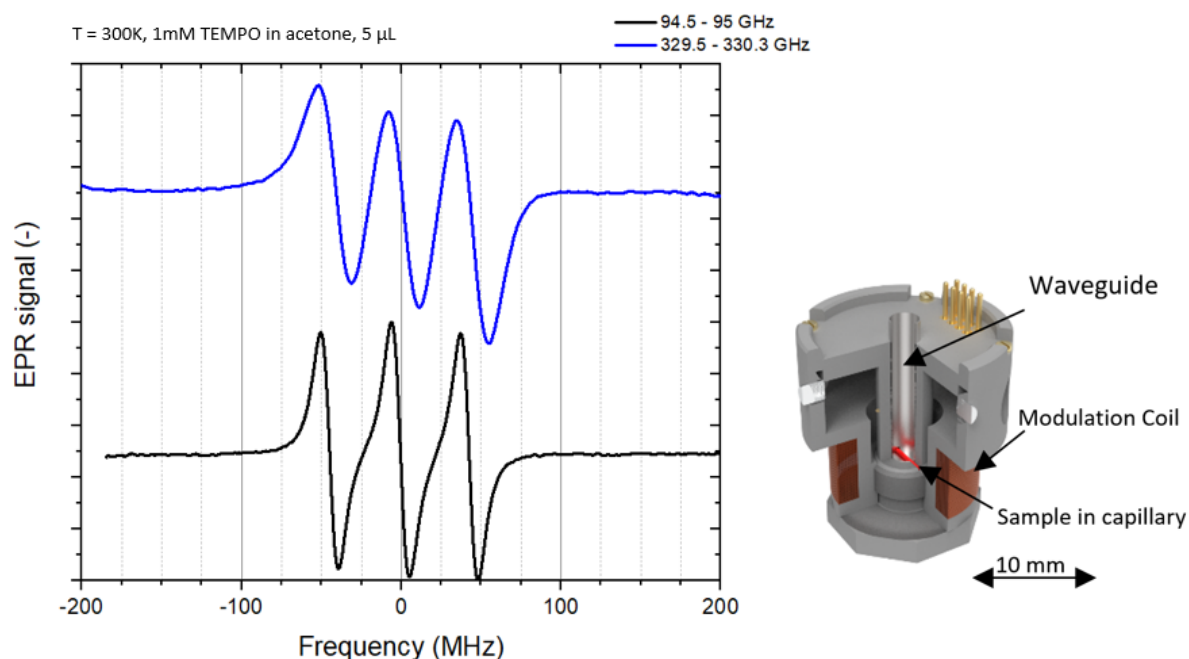
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Nitroxide radicals at high-field electron paramagnetic resonance: paving the way to DNP

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The study of organic nitroxide radicals is very important for both Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance. In our work, we present the first data of the nitroxide radical (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl TEMPO obtained with rapid scan EPR spectrometer at very high field. The measurement were obtained with our novel liquid cell sample holder together with a broadband EPR spectrometer based on rapid frequency scans that operates at frequencies from 80 GHz to 1100 GHz, at temperatures from 1.8 K to 300 K, and at magnetic fields up to 16 T. The successful study of such radicals in high magnetic fields is a necessary step in understanding and optimizing the nuclear polarization efficiency and developing spin polarization agents for Dynamic Nuclear Polarization.



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Electron spin resonance of defects in the organic spin chains compounds (o-DMTTF)₂X

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Defects in spin chains were a subject of great interest over the last decades. The spin-Peierls systems like the organic spin chains (o-DMTTF)₂X (X=Br, I, Cl) have an S=0 ground state [1]. However it is known [2] that a break in the translational symmetry can induce an S=1/2 ground state made by hundreds of spins of the chain. At low temperature paramagnetic signals are often observed and commonly attributed to extrinsic impurities.

By means of Electron Paramagnetic Resonance of (o-DMTTF)₂X, we show that the paramagnetic signal at low temperature is intrinsic to the chain. Despite an important concentration of spins, we observed long relaxation times and quantum coherence by performing Rabi oscillations on this two levels N-body system [1]. These characteristics are compatible with quantum information processing. We present in this poster the role of isotropic Heisenberg exchange interaction in the reduction of the relaxation effect due to the spin nuclei bath.

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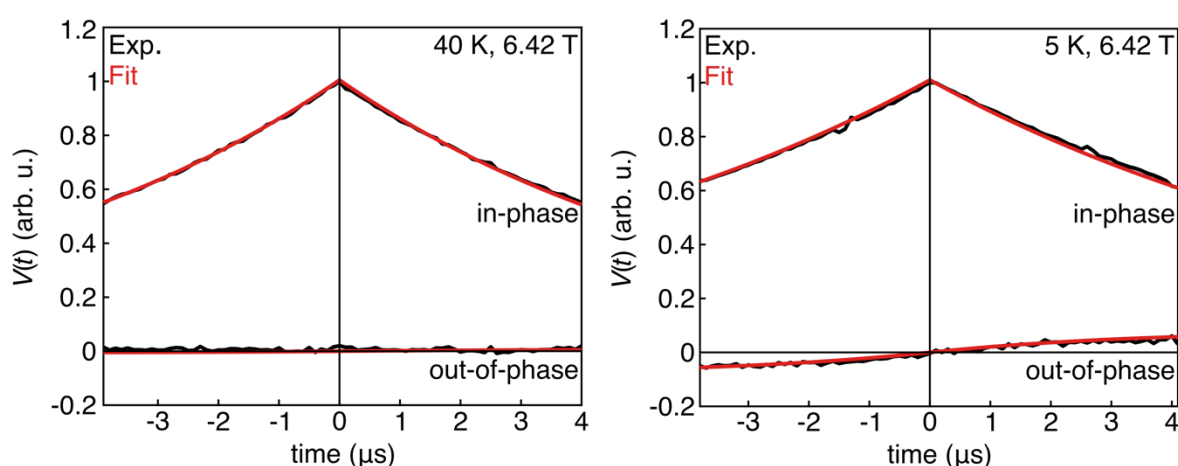
Polarization-dependent phase effect on low-temperature DEER spectroscopy

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Pulse electron paramagnetic resonance (EPR) spectroscopy, particularly those methods that measure dipolar couplings, are valuable for resolving protein structures. Among these is double electron–electron resonance (DEER) spectroscopy which measures the magnetic dipolar coupling between two radicals in the nanometer range, often on spin-labeled proteins. Such experiments are commonly conducted in the high-temperature regime, where the thermal polarization of the spins is minimal. In this regime, the DEER background signal has a uniform distribution of phases resulting in a single exponential decay function. To develop a more complete understanding of the spin dynamics underlying DEER, we have extended the theory beyond this limit to examine how these dynamics are affected in a highly polarized environment (low temperatures and high fields). This work has led to the discovery of a polarization dependent out-of-phase effect on the DEER signal, with a maximal magnitude of 5% of the in-phase signal. Here we characterize the polarized phase dependence through analytical derivation, numerical simulation, and experimental measurements using monoradical and biradical nitroxides at several fields and temperatures. While the effect comprises only a fraction of the overall DEER signal for these experiments, it highlights a novel aspect of the fundamental spin physics underlying DEER spectroscopy.



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EPR Signatures of Grafted V(IV) Sites Reveal the Clustered Nature of Silanols on Partially Dehydroxylated Silica Surfaces

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Amorphous silicas with hydroxyl-terminated surfaces are widely used as supports for chromatographic separations, and to disperse active sites consisting of single metal atoms or nanoparticles for applications in catalysis. Anchoring a paramagnetic probe molecule, VCl_4 , onto a silica surface was explored as a strategy to study the spatial distribution of the hydroxyl groups which often serve as anchoring points for surface modifiers. Thermal pretreatment is often proposed to lead to “isolated” silanols, which can be modified to generate non-interacting grafted sites. However, spatial isolation is usually inferred from an absence of evidence. In this study, an amorphous non-porous silica pretreated at 500 °C followed by reaction at room temperature with VCl_4 was studied by continuous wave Electron Paramagnetic Resonance (EPR) spectroscopy. The grafted $\equiv\text{SiOVCl}_3$ sites show clear signs of strong spin-spin coupling between the unpaired spins of adjacent V(IV) centers. The resulting short electron spin relaxation times cause the EPR spectral width to change dramatically as a function of temperature. At room temperature, the EPR signals are broadened beyond detection, but can be observed upon cooling to 20 K. The extent of spin-spin coupling is somewhat reduced by severe dilution of the paramagnetic centers. However, even at low surface V(IV) densities, the EPR spectrum experiences considerable broadening, indicating that the silanols are clustered. A semi-quantitative analysis allows estimation of the sizes of the silanol patches. ^1H - ^1H Double-Quantum Single-Quantum MAS NMR further corroborates the co-location of silanols. These findings demonstrate an approach which could be used to characterize the distribution of clustered paramagnetic centers that, under certain conditions, cease to generate measurable EPR signals. This study also suggests that the widely accepted strategy of thermal pretreatment of silica may not be sufficient to generate isolated hydroxyls.

An Advanced EPR Investigation of the *p*-Xylene Oxidation Process

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The catalytic oxidation of *para*-xylene to terephthalic acid (pTA) is one of the most important industrial-scale processes to modern-day consumers. Its primary use in the co-polymerisation with ethylene glycol to produce polyethylene terephthalate (PET) is responsible for food and drinks packaging, fabrics and upholstery, and numerous polymer blends, all of which are encountered by millions on a daily basis. pTA is generated on a Mt p.a. scale at over 60 sites globally and has incredibly high conversion, selectivity and purity. But despite the extremely well-refined process employed on an enormous industrial scale, some of the underlying mechanistic and structural aspects of the catalysis remain elusive.

The homogeneous catalytic mixture of Co, Mn and Br salts in aqueous acetic acid media is challenging to study for most characterisation techniques due to the harsh operating conditions and vast array of potential organic radical and paramagnetic transition metal intermediates. In this case, EPR is an extremely attractive spectroscopic technique to study this system. However, it is surprising to learn that very few examples of CW EPR applied to study this process have been published to date. Herein, we present a more comprehensive investigation into the underlying catalysis using a variety of CW and pulsed EPR techniques, including the application of spin trapping to identify radical intermediates, CW linewidth analysis as a probe of changing catalyst coordination sphere, and 3 pulse ESEEM as an empirical method of determining catalyst structure.

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EPR investigations on Cu(II) pairs in DUT-49(Cu) MOF to elucidate the magnetic coupling and Xenon adsorption properties

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Metal-Organic frameworks (MOFs) are the promising class of materials for a wide range of applications due to their reported features such as high surface area, crystal integrity, structural diversity, pore tunability and permanent porosity.^{1,2} EPR has been investigated on MOF systems for various fields such as photo and electrocatalytic applications, gas and liquid adsorption, magnetic properties, structural interrogation and breathing effects.^{1,2} Herein, we investigated the flexible DUT-49(Cu) MOF material by means of EPR spectroscopy to understand its exchange coupling (J) in the Cu(II) paddlewheel unit and the impact of Xenon adsorption on the structural phase transformation. The 'J' value fitted using the Bleaney-bowers equation² is found to be -161 cm⁻¹, and its sign is attributed to an antiferromagnetic coupling of the Cu(II) dimer in the paddle wheel. Further, *in situ* EPR studies on Xenon ad- and desorption at 155 K in the 0 to 60 kPa pressure range show the closed, mixed, open - pore hysteresis from the local view of the paddlewheel units. The spin Hamiltonian parameters are found to be $g_{\parallel} = 2.390(3)$, $g_{\perp} = 2.085(5)$ and $D = -10(1)$ GHz for the Cu(II) dimer at 291 K while an additional Cu(II) impurity species present in the DUT-49(Cu) MOF has $g_{\parallel} = 2.266(2)$, $g_{\perp} = 2.038(2)$, $A_{\parallel} = 569(3)$ MHz and $A_{\perp} = 95(3)$ MHz at 7 K.

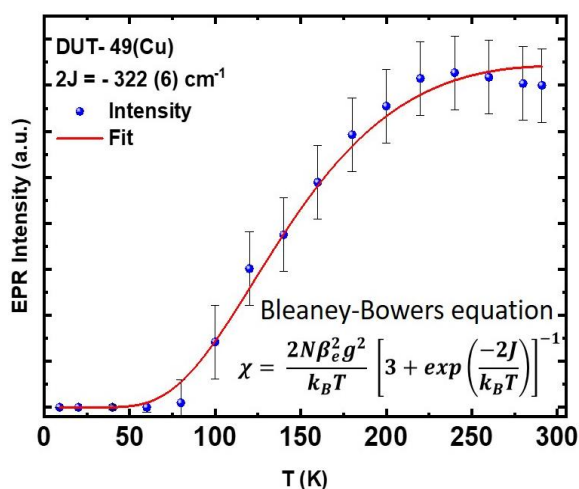


Fig: EPR intensity of Cu pairs measured at X-band frequencies.

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Triplet fullerene spin labels for pulsed dipolar EPR spectroscopy

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Pulsed dipolar EPR spectroscopy has been proved a valuable tool for extracting structural and dynamic data from spin-labeled biomolecules. Since widely used nitroxide spin labels give insufficient sensitivity, new kinds of labels appear intended to improve data quality. Recently, our group proposed triplet fullerene as a perspective spin label for DEER distance measurements [1]. Triplet fullerene hyperpolarization reduces DEER accumulation time by a factor of 10-1000 compared to nitroxide radicals, which is greatly important for acquiring long distances. One of our problems today is the development of fullerene-based spin label featuring the outstanding properties of pristine fullerene and applicable to measure distances in water-soluble biomolecules.

In this work we attempted different strategies to achieve high EPR signal and long phase memory times for water-soluble fullerene derivatives. We characterize the derivatives using EPR at 20 K and UV-vis spectroscopy and compare to pristine fullerene. Derivatization of fullerenes does not lead to full dissolution in water to monomers, so derivatives exhibit poor triplet EPR signal in water. To improve their water solubility and obtain magnetic properties we employed non-covalent formation with gamma-cyclodextrins. The fullerene:cyclodextrin complexes are dissolved then to monomers and feature triplet EPR spectra as of pristine fullerene dissolved in toluene. Similar to nitroxides, transverse relaxation at low temperatures is determined by nuclear spin diffusion, so deuteration increases phase memory times. Moreover, we implemented several methods of pulsed dipolar EPR on model fullerene-nitroxide and fullerene-trityl dyads, such as relaxation-induced dipolar modulation enhancement (RIDME) and laser-induced magnetic dipolar spectroscopy (LaserIMD), identifying main advantages and disadvantages of these methods applying to triplet fullerene spin labels.

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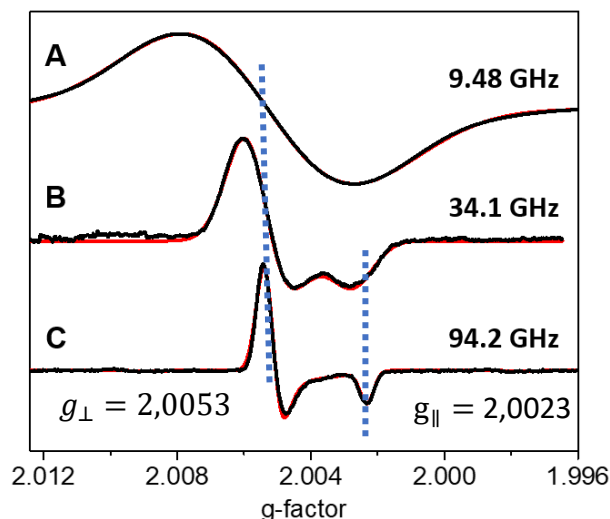
EPR characterization of two new bacterial formate dehydrogenases for CO₂ valorization

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Nowadays one of the biggest environmental challenge is the bioremediation of atmospheric CO₂. Biocatalytic reduction of CO₂ into formate by microbial formate dehydrogenases (FDHs) is very promising [1]. In this work, we present the EPR characterization of two similar FDHs, named ForCE1 and ForCE2, from the soil bacterium *Bacillus subtilis*. These enzymes belong to the Mo/W-*bis*PGD (i.e. pyranopterin guanosine dinucleotide) superfamily, previously referred as the DMSOR family, widespread among prokaryotes [2]. These two FDHs appear to be of great scientific interest for the following reasons. First, sequence analyses reveal that they belong to a still uncharacterized family of FDHs. Secondly, they display a high oxygen tolerance, an auspicious feature for potential biotechnological purposes. Finally, how these enzymes are integrated in the metabolism of this aerobic organism remains to be established, leaving an open door for new biological discoveries.



The catalytic core of ForCE1 and ForCE2 is composed of two subunits. From sequence analysis, the largest one (ForC) is predicted to coordinate five iron-sulfur clusters and a Mo-*bis*PGD whereas ForE does not appear to house any cofactor. By combining redox potentiometry and EPR spectroscopy, we were able to characterize the EPR signatures and the redox properties of several paramagnetic cofactors in the purified enzymes. These are assigned to three [4Fe-4S] clusters, one [2Fe-2S] and a Mo(V) species. In addition, an unexpected intense radical signal was also detected. Its identification using a multi-frequency EPR approach allowed us to fully elucidate the catalytic function of these enzymes.

To conclude, two representatives of an uncharacterized FDH subfamily display astonishing properties supporting further EPR and electrochemical investigations.

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Globin-33, a heme-based sensor in *Caenorhabditis elegans* with unusual characteristics as revealed by EPR spectroscopy

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Although members of the globin protein family exist in various shapes and sizes (monomeric, multimeric and chimeric), they all share the so-called *globin-fold*, a typical three-on-three or two-on-two helical sandwich forming a hydrophobic crevice in which a heme is bound to a proximal histidine residue. The structural heterogeneity is reflected in a wide functional diversity of globins ranging from O₂ binding, to roles in the detoxification of reactive nitrogen and oxygen species and redox transfer. Surprisingly, 34 globin-related (glb) genes were discovered in the nematode *Caenorhabditis elegans* [1]. Among those, glb-33 is the largest of its kind and is expressed in the nervous system. The gene product (GLB-33) was biochemically characterized as a membrane-bound, putative globin-coupled neuropeptide receptor [2]. Starting from the N-terminus, the first 372 amino acids (AAs) are modelled as a 7 alpha-helical transmembrane domain, typical of a G protein-coupled receptor, and the remaining 170 AAs as a heme-containing globin domain (GD). The GD has a particularly hydrophobic heme pocket that shows a high affinity for O₂ and oxidizes fast to a ferric Fe(III) heme state with a hydroxide coordinated to the heme iron at the distal side of the heme at neutral pH. Moreover, the GD possesses an extraordinary fast nitrite reductase (NiR) activity compared to the majority of globins. In this work, CW EPR was complemented with different pulsed EPR and ENDOR techniques to characterize the pH-dependence of ferric GLB-33GD and the effect of addition of nitrite to ferric GLB-33D at different pH values. Furthermore, the nitrosyl ferrous Fe(II) form of the GD, a reaction product that is formed as a consequence of NO rebinding at the ferrous heme after the NiR activity, was studied. All results will be compared to available data of different globins, stressing the unique properties of GLB-33GD in addition to a discussion of common characteristics.

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Factors Influencing Cu^{II}-Chelate Labelling at Double-Histidine Motifs for Pulse Dipolar EPR Applications

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Electron paramagnetic resonance (EPR) distance measurements are making increasingly important contributions to studies of biomolecules underpinning health and disease by providing highly accurate and precise geometric constraints.¹ Combining double-histidine (dH) motifs with Cu^{II} spin labels shows promise to further improve precision of distance measurements,² and appeals in proteins containing essential cysteines which can interfere with thiol-specific labelling. However, the approach is vulnerable to low binding-affinity.³ These dissociation constants (K_D) were previously investigated via modulation depths of relaxation induced dipolar modulation enhancement (RIDME) EPR distance experiments,⁴ and demonstrated measurements at sub- μ M protein concentrations in orthogonally labelled Cu^{II}-nitroxide systems. These findings opened avenues of subsequent investigation regarding optimisation of Cu^{II} labelling in tetra-histidine constructs. Herein, modulation depth quantitation in Cu^{II}-Cu^{II} RIDME to simultaneously estimate a pair of non-identical independent K_D values in a model protein is addressed.⁵ Furthermore, a general speciation model to optimise Cu^{II} labelling efficiency in dependence of pairs of identical or disparate K_D values is developed. Lastly, the influence of pH and competitor divalent metal ions on the efficiency of Cu^{II} labelling at dH motifs is investigated via isothermal titration calorimetry (ITC) and Cu^{II}-nitroxide RIDME measurements.

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High frequency, high sensitivity EPR probe design optimized using the CST STUDIO Suite

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In this paper, we describe ongoing work to design, optimise, and test new sample probes for high concentration sensitivity pulsed EPR using an existing kW spectrometer operating at 94 GHz (HiPER).

If concentration sensitivity is the primary goal, then at high frequencies and high power levels it can be very beneficial to use simple single-mode transmission line structures with reflective backshorts, instead of traditional cavities. These structures offer easy sample handling and relatively large sample volumes (compared to the wavelength), which maximises concentration sensitivity, for a given bandwidth. They are particularly easy to operate in induction mode, where the sample is illuminated by a linearly polarised beam, but where the signal is detected from the orthogonal linearly polarised state. This has the huge advantage of providing a large degree of isolation between the transmitted pulse and the detection system, whilst maintaining sensitivity, but hugely reducing the requirements imposed on the receiver protection system.

For frozen or powder samples, these types of sample holders act as weak resonant structures, where there is a resonance between the top of the sample and the reflective backshort. The Q of the structure is then very approximately given by $2 \pi \epsilon n$ where ϵ is the dielectric constant of the sample and n is the number of half wavelengths in the sample (at the resonance frequency). In practice using HiPER, sample volumes are normally chosen to give a $Q \sim 100$ and resonator bandwidths close to 1 GHz, but it is relatively easy to adapt the set-up depending on the amount of sample available and the bandwidth required. The position and orientation of the backshort, which incorporates a weak roof mirror, can then be used to either maximise signal or maximise isolation between transmitter and detector.

In this study we use the CST Microwave STUDIO suite, to investigate how these structures may be optimised for different applications and determine effective conversion factors, filling factors and bandwidths. We investigate smooth walled circular guide, corrugated guide and bimodal structures, where a higher order mode is trapped in the sample, and examine the trade-offs between bandwidth, volume and finesse for a given resonant structure. In particular, we show there can be advantages in using corrugated guide structures as they have better filling factors than smooth guide, and offer reduced scattering to the orthogonal linearly polarised state. For certain samples this can lead to a significant increase in sensitivity.

Self-Organisation of Copper Species at the Surface of Cu₂O/TiO₂ Systems During H₂ Evolution Reaction: A Combined Investigation by EPR and Optical Spectroscopy

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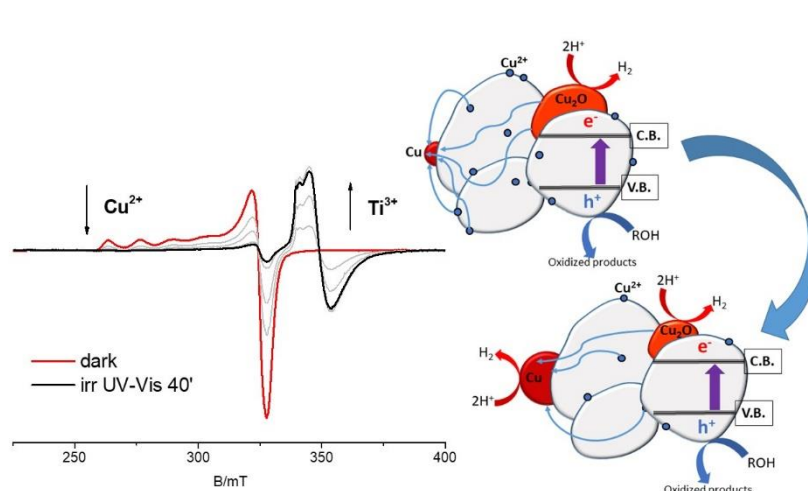


Figure 1. Sketch representation of the systems described (left) and evolution of the related paramagnetic species (right) during the photocatalytic process of H₂ production.

The Cu₂O/TiO₂ system represents a material of great interest for the high efficiency in the H₂ evolution reaction (HER) [1,2]. However, Cu₂O, especially in acidic environment, undergoes a rapid degradation via leaching processes [3]. Aim of this work is the investigation of the Cu-containing species evolution during the HER process [4].

The joint application of CW-EPR and optical spectroscopy has shown that a remarkable oxidation of the cuprous oxide already occurs during the preparation step of the photocatalyst, leading to the formation of surface dispersed Cu(II) ions. Only a fraction of these species is detected by EPR while a second fraction is in the form of diamagnetic dimers or oligomers. These centres become EPR visible upon contact with the liquid phase during the HER due to the coordination with the solvent. The spectroscopic investigation performed in catalytic conditions, as a sort of “operando” characterization, has also pointed out the subsequent reduction of Cu²⁺ ions to the metallic form (Cu⁰, identified by optical spectroscopy) together with the formation of Ti³⁺ centres in the oxide matrix (Fig. 1). As a consequence of this process, it is possible to claim that the as prepared material only represents a pre-catalyst which is modified during irradiation leading to the real working system. This catalyst however is partially inactivated by the metallic copper formed during the reaction, which is in fact less active than the initial Cu₂O.

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