

The 51st Annual International Meeting
of the
Electron Spin Resonance Group
of the
Royal Society of Chemistry



51st RSC ESR Conference

Book of Abstracts

8th April – 12th April 2018
Queen Mary, University of London

Sunday 8th April

9:00 - 16:00 Arrival

16:00 - 18:00 Registration

18:00 - 20:00 BBQ Dinner

20:00 - 00:00 Free Evening

Monday 9th April

9:00 - 9:10 Conference opening

Session Chair: Damien Murphy 9:10 - 9:50 Klaus Lips (Plenary) 9:50 - 10:10 Till Biskup 10:10 - 10:30 Daniel Rodrigues Cardoso

10:30 - 10:55 Coffee break

Session Chair: Etienne Goovaerts 10:55 - 11:25 Dama Freedman (Invited) 11:25 - 11:45 Alessandro Lodi 11:45 - 12:05 Maria Fittipaldi 12:05 - 12:25 Shang Da Jiang

12:25 - 13:55 Lunch

Session Chair: Sabine van Doorslaer 13:55 - 14:25 Paul Walton (Invited) 14:25 - 14:45 Dima Svistunenko 14:45 - 15:05 Nicole Erlenbach 15:05 - 15:25 Mario Chiesa 15:25 - 15:45 Ilya Kuprov
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15:45 - 16:10 Coffee break

16:10 - 17:30 Poster Session 1 (odd numbers)

17:30 - 17:40 Bruker Laudatio 17:40 - 18:40 Bruker Thesis Lecture Audrey Bientaft

18:40 - 20:30 Dinner

20:30 - 20:40 Bruker Prize Laudatio 20:40 - 21:40 Bruker Prize Lecture Sabine van Doorslaer 21:30 - 00:00 Bruker Reception

Tuesday 10th April

9:00 - 9:10 Announcements

Session Chair: Eric McInnes 9:10 - 9:50 Daniella Goldfarb (Plenary) 9:50 - 10:10 Stephan Pribitzer 10:10 - 10:30 Martina Cirulli 10:30 - 10:50 Michael Slota

10:50 - 11:15 Coffee break

Session Chair: Eric McInnes 11:15 - 11:45 Ines Garcia-Rubio (Invited) 11:45 - 12:05 Leah Weiss 12:05 - 12:25 Melissa Van Landeghem 12:25 - 12:45 Katherina Keller
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12:45 - 14:15 Lunch

14:15 - 00:00 Free Afternoon and Evening 14:15 - 16:15 ESR Group Committee Meeting and AGM
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Wednesday 11th April

9:00 - 9:10 Announcements

9:10 - 9:20 Feher In Memoriam Session Chair: Wolfgang Lubitz 9:20 - 10:00 Marina Bennati (Plenary) 10:00 - 10:20 Michal Zalibera 10:20 - 10:40 Joris van Slageren 10:40 - 11:10 Emma Richards (Invited)

11:10 - 11:35 Coffee break

Session Chair: Gunnar Jeschke 11:35 - 11:55 Olav Schiemann 11:55 - 12:15 Alice Bowen 12:15 - 12:35 Alberto Collauto 12:35 - 12:55 Christos Pilotas

12:55 - 14:25 Lunch

Session Chair: Mark Newton 14:30 - 15:00 Alan Drew (Invited) 15:00 - 15:20 Jason Sidabras 15:20 - 15:40 Graham Smith 15:40 - 16:00 Jeremy Good

16:00 - 16:25 Coffee break

16:25 - 17:55 Poster Session 2 (even numbers)
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Session Chair: Janet Lovett 17:55 - 18:15 Alistair Fielding 18:15 - 18:35 Vasily Oganesyan

18:35 - 18:45 IES Laudatio 18:45 - 19:45 IES Fellowship Wolfgang Lubitz

20:00 - 22:00 Banquet

22:00 - 00:00 JEOL Reception

Thursday 12th April

9:00 - 9:10 Announcements

Session Chair: Graham Smith 9:10 - 9:50 Mark Newton (Plenary) 9:50 - 10:10 Jonathan Breeze 10:10 - 10:30 Floriana Tuna 10:30 - 10:50 Konstantin Herb

10:50 - 11:15 Coffee break

Session Chair: David Collison 11:15 - 11:45 Stephen Sproules (Invited) 11:45 - 12:05 Haleh Haeri 12:05 - 12:25 Stephan Rein 12:25 - 12:45 Janne Soetbeer

12:45 - 12:50 Conference closure
12:50 - 12:55 2019 Announcement
12:55 - 14:15 Lunch

14:15 - 00:00 Departure



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Sunday, 8th April

16:00 – 18:00 Registration

18:00 – 20:00 BBQ dinner

20:00 – 00:00 Free evening

Monday, 9th April

9:00 – 9:10	Maxie Roessler & Enrico Salvadori	Welcome
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Session 1	Chair: Damien Murphy
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9:10 – 9:50	Klaus Lips Plenary Speaker	Ultra-Sensitive Operando Detection of Paramagnetic States in Silicon Solar Cells
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9:50 – 10:10	Till Biskup	The path to enlightenment: What TREPR teaches us about electronic structure, morphology, and flexibility of conjugated polymers
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10:10 – 10:30	Daniel Cardoso	EPR studies on the photoinduced electron-transfer in viologens-tetraarylborate complexes
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10:30 – 10:55	Coffee Break
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Session 2			Chair: Etienne Goovaerts
10:55 – 11:25	Danna Friedman Invited Speaker	Molecular Design and Synthesis as a Vector for Understanding Electron Spin Relaxation	
11:25 – 11:45	Alessandro Lodi	ESR Spectroscopy: Monoradical and Biradical as building block for magnetic Graphene Nanoribbon	
11:45 – 12:05	Maria Fittipaldi	Magnetic Nanoparticles in Bioreactors: host-guest characterization by EPR and Mössbauer Spectroscopies	
12:05 – 12:25	Shang Da Jiang	Endohedral Fullerenes as Molecular Qubits	
12:25 – 13:55	Lunch		
Session 3			Chair: Sabine van Doorslaer
13:55 – 14:25	Paul Walton Invited Speaker	Multi-frequency EPR spectroscopy and Angular Overlap Model Analysis of the Copper Active Site of Lytic Polysaccharide Monooxygenases	
14:25 – 14:45	Dima Svistunenko	H ₂ O ₂ activation of the dye-decolorizing peroxidase DtpA from Streptomyces lividans – is it one Compound I or two of them?	
14:45 – 15:05	Nicole Erlenbach	Small dsDNA as model systems for orientation selective pulsed EPR	
15:05 – 15:25	Mario Chiesa	The Unusual Chemistry of Group XII Elements in Zeolites. An Electron Magnetic Resonance Investigation.	
15:25 – 15:45	Ilya Kuprov	It's not just $1/r^6$: magnetic anisotropy effects on lanthanide induced paramagnetic relaxation enhancement	





15:45 – 16:10 Coffee Break

16:10 – 17:30 Poster Session 1 Odd Numbers

Bruker Thesis Prize Lecture

17:30 – 17:40 Ilya Kuprov Bruker Thesis Prize Laudatio

17:40 – 18:40 Audrey Bienfait **Bruker Thesis Prize 2018**
Magnetic resonance with quantum microwaves

18:40 – 20:30 Dinner

Bruker Prize Lecture

20:30 – 20:40 Gunnar Jeschke Bruker Prize Laudatio

20:40 – 21:40 Sabine van Doorslaer **Bruker Prize 2018**
Hyperfine companions on a journey through the world of (bio)materials

21:40 – 00:00 Bruker Reception

Tuesday, 10th April

9:00 – 9:10 Organising Committee Announcements





Session 4			Chair: Eric McInnes (+ JEOL Prize Competition)		
9:10 – 9:50	Daniella Goldfarb Plenary Speaker	Exploring Protein's Conformations in Cells with Gd(III) Spin Labeling			
9:50 – 10:10	JEOL Prize Stephan Pribitzer	Two-dimensional distance correlation maps from pulsed triple electron resonance (TRIER) on proteins			
10:10 – 10:30	JEOL Prize Martina Cirulli	Mechanically Interlocked Molecules: The Effect of the Mechanical Bond on the Magnetic Properties of Transition Metals Complexes			
10:30 – 10:50	JEOL Prize Michael Slota	Magnetic edge states, spin dynamics and coherent manipulation of molecular graphene nanoribbons			
10:50 – 11:15	Coffee Break				
Session 5			Chair: Eric McInnes (+ JEOL Prize Competition)		
11:15 – 11:45	Ines Garcia-Rubio Invited Speaker	Studying the structural changes of human Apoptosis Inducing Factor using spin labels			
11:45 – 12:05	JEOL Prize Leah Weiss	Spin-signatures and dynamics of exchange coupled triplet excitons from singlet fission			
12:05 – 12:25	JEOL Prize Melissa Van Landeghem	When stronger magnets don't help: Methods for disentangling overlapping high-field EPR spectra illustrated in record organic solar cell blend PBDB-T:ITIC			
12:25 – 12:45	JEOL Prize Katherina Keller	Metal centres in RIDME spectroscopy: methodology and application			
12:45 – 14:15	Coffee Break				





14:15 – 00:00 Free Afternoon

- RSC ESR Group Committee
 - National Facility Steering Committee
 - Other Meetings
-

Wednesday, 11th April

9:00 – 9:10	Organising Committee	Announcements
Session 6	Chair: Wolfgang Lubitz	
9:10 – 9:20	Wolfgang Lubitz	Feher <i>in memoriam</i>
9:20 – 10:00	Marina Bannati Plenary Speaker	From EPR to DNP: Recent Developments in ENDOR and Liquid State DNP to Study Biomolecules
10:00 – 10:20	Michal Zalibera	Excited triplets of endohedral nitride cluster fullerenes: EPR/ENDOR
10:20 – 10:40	Joris van Slageren	EPR investigations of potential molecular quantum bits
10:40 – 11:10	Emma Richards Invited Speaker	Low-Valent Nickel(I) Complexes Stabilised by RE-NHCs: Synthesis, EPR/DFT Studies and Catalytic Activity
11:10 – 11:35	Coffee Break	





Session 7		Chair: Gunnar Jeschke
11:35 – 11:55	Olav Scheimann	Studying Conformations of Oligonucleotides with Pulsed Dipolar Spectroscopy
11:55 – 12:15	Alice Bowen	Exploring reliable distance measurements and dipolar correlations in an orthogonally labelled three-spin system
12:15 – 12:35	Alberto Collauto	In-cell PELDOR spectroscopy on spin-labelled RNAs
12:35 – 12:55	Christos Pliotas	Mechanical activation of an ion channel by chemical modification of pressure sensitive nano-pockets
12:55 – 14:25 Lunch		
Session 8		Chair: Mark Newton
14:30 – 15:00	Alan Drew Invited Speaker	Temporal mapping of excitonic wavefunctions with carbon specificity
15:00 – 15:20	Jason Sidabras	Uniform Field Resonators for Correlation Spectroscopy Methods at Q-band
15:20 – 15:40	Graham Smith	Meeting the Sensitivity Grand Challenges in Pulsed EPR
15:40 – 16:00	Jeremy Good	Cryogen Free Superconducting Magnets for Solid State NMR and DNP Applications
16:00 – 16:25 Coffee Break		





16:25 – 17:55	Poster Session 2	Even Numbers
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Session 9	Chair: Janet Lovett
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17:55 – 18:15	Alistair Fielding	A Bifunctional Spin Label for Ligand Recognition on Surfaces
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18:15 – 18:35	Vasily Oganessian	Rn - a spin label with limited internal mobility sensitive to protein dynamics: evidence from a combined EPR and Molecular Dynamics simulation study
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International EPR Society Speakers

18:35 – 18:45	Thomas Prisner	IES Laudatio
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18:45 – 19:45	IES Fellowship Wolfgang Lubitz	The Spin as Probe for Structure and Function in Metal Biocatalysis
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20:00 – 22:00	Banquet
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22:00 – 00:00	JEOL Reception
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Thursday, 12th April

9:00 – 9:10	Organising Committee	Announcements
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Session 10	Chair: Graham Smith	
9:10 – 9:50	Mark Newton Plenary Speaker	Taming defects in diamond
9:50 – 10:10	Jonathan Breeze	Continuous-wave room-temperature maser using NV centres in diamond
10:10 – 10:30	Floriana Tuna	NO ₂ adsorption in porous metal organic frameworks (MOFs) investigated by electron paramagnetic resonance
10:30 – 10:50	Konstantin Herb	Double resonance calibration of g factor standards: Carbon fibers as a high precision standard
10:50 – 11:15	Coffee Break	
Session 11	Chair: David Collison	
11:15 – 11:45	Stephen Sproules Invited Speaker	Iron One
11:45 – 12:05	Haleh Haeri	Multi frequency EPR study of novel paramagnetic diazadiene complexes of alkali metals lithium and sodium
12:05 – 12:25	Stephan Rein	SpecProFi: A new comprehensive EPR data processing and fitting framework
12:25 – 12:45	Janne Soetbeer	How to make the most of π pulses: dynamical decoupling of nitroxides
12:45 – 12:55	Maxie Roessler Stephen Sproules	Conference closure and 2019 Meeting Announcement
12:55 – 14:15	Lunch and Departure	





List of Posters

Adam Brookfield	EPSRC National UK EPR Facility and Service	P1
Alexey Potapov	High field pulse EPR for structural studies of CCR4-NOT nuclease complex	P2
Angeliki Giannoulis	Trityl tags for W-band distance measurements in proteins	P3
Anokhi Shah	A Gadolinium EPR Label for Selective Protein Conjugation: Minimising the Zero-field Splitting and the Tether Length	P4
Bela Bode	Insights into histidine-rich glycoprotein from electron paramagnetic resonance spectroscopy	P5
Charles Larminie	Pulsed Dipolar Spectroscopy exploiting photogenerated triplet states – a model peptide study	P6
Claudia Tait	Design of an AWG-based Q-band EPR spectrometer system for pulse EPR	P7
Dana Dvoranová	Insights into visible-light activity of g-C ₃ N ₄ /TiO ₂ nanopowder photocatalysts	P8
Daniel Klose	Structural Characterization of low-coordinated Ti(III) alkyl species by Pulsed EPR Spectroscopy	P9
David Keeble	EMR of photovoltaic non-fullerene acceptor polymer blends	P10
David Keeble	EPR of Fe ³⁺ -centres in ferroic titanate oxides	P11
Denisa Darvasiová	EPR and UV-vis-NIR spectroelectrochemistry of five-coordinate manganese(III) complex with a salen type ligand, a catalyst of secondary alcohol oxidation	P12





Dominik Kubicki	Phase segregation in transition metal (Co^{2+} , Mn^{2+}) doped lead halide perovskites from solid-state NMR	P13
Edmund Little	Investigations into Quantum Interference Phenomena in Supramolecular Assemblies Using Pulsed Dipolar Spectroscopy	P14
Federico Lombardi	Characterization of Spin Dynamics in Open-Shell Aromatic Radicals through EPR spectroscopy	P15
Frauke Breitgoff	Broadband excitation for distance measurements between Cu(II) centers	P16
Gabriel Moise	Transient EPR study of the photo-excited triplet state of a series of linear palladium (II) porphyrin oligomers	P17
Gabriela Ionita	Identification of radicals formed during the riboflavin/UV-A-induced collagen crosslinking for the treatment of keratoconus	P18
Gabriele Stevanato	Radical geometry: a key to efficient Dynamic Nuclear Polarization.	P19
Gert Denninger	What do we mean by g-factor in exchange coupled electron spin systems?	P20
Gunnar Jeschke	Using Distance Distribution Information in Integrative Structural Biology	P21
Irina Ritsch	Orientation-Selective RIDME with Cu(II) -Nitroxide Spin Pairs using Chirped Pulses	P22
Ivan Sudakov	Photodegradation processes in fullerene-free organic solar cells investigated by Electron Paramagnetic Resonance	P23
Ivan Timofeev	EPR study of ribosomal assemblies. Monte Carlo analysis of DEER data	P24
Jakub Mrozek	Engineering entanglement in molecular spin systems	P25





Janet Lovett	DEER distance measurements with Y@C ₈₂ spin labels	P26
John Wright	EPR investigations of ubiquinone reduction by respiratory complex I in native and non-native membrane systems	P27
Joshua Wort	Dissociation Constant Determination via RIDME Modulation-depth Quantitation	P28
Kaltum Abdiaziz	A new spectroelectrochemical technique to study (bio)catalysts	P29
Katharina Rudi	Conformational dynamics of mVDAC1 and the influence of tBid studied by SDSL with pulse EPR and MD simulation	P30
Katherine Fisher	EPR of lanthanide complexes: exploring the consequences of ligand induced anisotropy	P31
Katrin Ackermann	Resolving the true distance distribution in homo-multimers	P32
Kevin Nys	New insights into the B-class dye-decolorizing peroxidases: An EPR study of the heme and the radical sites in a DyP from <i>K. pneumoniae</i>	P33
Lucia Gigli	Integration of DEER data in Maximum Occurrence analysis	P34
Luis Fabregas	Processing methods for spectra and two-dimensional distance correlation maps from pulsed triple electron resonance (TRIER)	P35
Lydia Nodarak	Pulsed EPR studies of an amide-based Sc(II) complex	P36
Magdalena Schumacher	Conformational changes of Channelrhodopsin-2 investigated by time-resolved EPR spectroscopy	P37
Mantas Šimėnas	Pulse EPR and ENDOR study of manganese doped [(CH ₃) ₂ NH ₂][Zn(HCOO) ₃] hybrid perovskite	P38





Maria Oranges	Identifying Intra-Monomer Distances by using PELDOR	P39
Michele Vonci	Electronic structure of three isostructural nine-coordinate lanthanide families with small crystal field splitting: a combined experimental and ab initio study	P40
Mohammad Samanipour	Elucidation of the mechanism of the intramolecular cyclisation of allyl 2-bromobenzyl ether by <i>in-situ</i> EPR spectroelectrochemistry and DFT calculations	P41
Nídia Almeida	Studying Dps–flavoprotein WrbA interaction using CW-EPR spectroscopy	P42
Niels Van Brempt	Nitrite reductase activity of GLB-33, a unique chimeric globin in <i>Caenorhabditis elegans</i> examined with EPR and UV-vis spectroscopy	P43
Nino Wili	Chirp echo FT EPR-detected NMR	P44
Peter Rapta	EPR spectroscopy and in situ EPR/UV-vis-NIR spectroelectrochemistry of nickel based macrocyclic complexes as potential catalysts for production of energetically rich materials	P45
Sabine Richert	Electronic Communication in Bis-Copper Porphyrin Oligomers	P46
Samuel Lenz	Spin dynamics of potential molecular qubits in thin films	P47
Steven Worswick	DEERNet – a deep neural network for DEER data processing	P48
Tufa Assafa	Orthogonal labelling strategies to study protein interaction networks	P49
Vincent Ching	Structural Characterisation of <i>Danio rerio</i> Cytoglobins	P50
Wei Song	Investigating the role of an arginine residue near the Fe-S cluster N2 in complex I	P51





William Myers	Reversible H ₂ coordination to a Fe(I) complex, monitored by ESR in solution and in the solid state	P52
Zainab Hafideddine	Spectroscopic analysis of myoglobin and neuroglobin immobilized on mesoporous materials	P53
Zuzana Barbierikova	TiO ₂ /Bi ₂ O ₃ heterojunction photocatalysts – visible light activity	P54





Official Sponsors of the RSC ESR Meeting 2018

The organisers are indebted to the following sponsors for their generous support:



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JEOL Student Prize



The RSC ESR Group Committee is pleased to announce the 21st Annual JEOL Prize Talk Competition, sponsored by JEOL.

This competition is open to any doctoral student (typically in year 2 or beyond) and 1st year post-doctoral scientists. Previous prize winners and those who gave a prize talk at the preceding meeting are ineligible to apply. These 15-minute lectures, scheduled for Tuesday morning, will be judged on the basis of both scientific content and delivery. The winner of the JEOL Prize 2018 will be announced at the JEOL Reception on Wednesday evening.

The following six lectures were selected by the Committee on the basis of the abstract submitted (in order of the programme):

Stephan Pribitzer ETH Zürich	Two-dimensional distance correlation maps from pulsed triple electron resonance (TRIER) on proteins
Martina Cirulli Queen Mary, University of London	Mechanically Interlocked Molecules: The Effect of the Mechanical Bond on the Magnetic Properties of Transition Metals Complexes
Michael Slota University of Oxford	Magnetic edge states, spin dynamics and coherent manipulation of molecular graphene nanoribbons
Leah Weiss University of Cambridge	Spin-signatures and dynamics of exchange coupled triplet excitons from singlet fission
Melissa Van Landeghem University of Antwerp	When stronger magnets don't help: Methods for disentangling overlapping high-field EPR spectra illustrated in record organic solar cell blend PBDB-T:ITIC
Katherina Keller ETH Zürich	Metal centres in RIDME spectroscopy: methodology and application





Bruker Prizes and Reception



Bruker Prize Lecture 2018 – Sabine van Doorslaer, University of Antwerp



Since 1986 Bruker BioSpin has generously sponsored an annual lectureship and prize, awarded to a scientist who has made a major contribution to the application of ESR spectroscopy in chemical or biological systems.

“The Bruker Prize 2018 of the Electron Spin Resonance Group of the Royal Society of Chemistry is awarded to Professor **Sabine Van Doorslaer**, University of Antwerp for her outstanding contributions in application-oriented method development and for cutting-edge studies of proteins, materials, and catalysts. Sabine Van Doorslaer applies a broad arsenal of advanced pulsed ESR techniques at different frequencies and analyses the spectra based on quantum-chemical computations in order to understand the spatial and electronic structure of paramagnetic systems. Thanks to

Sabine it became known how structurally diverse the heme centres of globins are and how this structural diversity is related to function – a field of research that is still very active and will no doubt be good for further surprises. The same methodology can be applied to the understanding of paramagnetic catalysts. Her collaborative work on asymmetric homogeneous catalysis by chiral Cu-salen complexes and on surface species in heterogeneous Ziegler-Natta catalysis stands out in this field. Sabine has contributed a number of fine papers on the measurement of small hyperfine couplings and on signal processing in electron spin echo envelope modulation spectroscopy already early in her career.

Beyond her research achievements, Sabine Van Doorslaer is a great teacher and has strongly contributed to the cohesion of our community and to collaboration within it. She is a regular and very much liked lecturer in summer schools of the European Federation of EPR Groups and has chaired the European COST Action on Advanced Paramagnetic Resonance Methods in Molecular Biophysics. Currently, she is President of European Federation of EPR Groups.”

– Prof. Gunnar Jeschke, ETH Zürich

The 2018 Bruker lecture “**Hyperfine companions on a journey through the world of (bio)materials**” will be delivered on Monday evening, followed by the Bruker reception.





Bruker Thesis Prize 2018 – Audrey Bienfait, Université Paris-Saclay

The ESR Group of the Royal Society of Chemistry and Bruker Corporation are pleased to announce the 4th Bruker ESR Thesis Prize, set up to recognize outstanding work by PhD students in the field of ESR Spectroscopy. The winner of the 2018 competition is **Audrey Bienfait** for her thesis completed at CEA-Saclay. Our expert panel of reviewers said of her work:

“This is the first experimental observation of the Purcell effect. When the Nature paper reporting the work was published, I immediately recognized its importance and made it the focus of one of my weekly EPR tutorials. The thesis demonstrates deep scholarship and understanding of this striking new perspective on spin relaxation. The scholarship covers a wide range of topics relevant to the key experiments and the theoretical background. There is good assessment of the relative effects of various experimental parameters. A prize lecture on this topic will be the highlight of the meeting.”



– Bruker Thesis Prize Reviewing Committee

“Nearly everyone in Magnetic Resonance had so far treated radiofrequency and microwave irradiation as “the B_1 field” – a one-way term in the spin Hamiltonian with a cosine in front and a tendency to complicate the mathematics. That is, of course, an approximation: in a good enough resonator the electromagnetic field is quantised, and a two-way quantum mechanical interaction exists between the spins and the electromagnetic field – a generalisation of the Zeeman effect. However, extraordinary extents of miniaturisation, electronic engineering and cooling are required to make it visible.

This work has accomplished the feat. It reports the first experimental observation of the Purcell effect – a two-way quantum mechanical interaction between the electromagnetic field of the resonator and the spins inside it. The effect is strong enough to be the dominant relaxation mechanism for the systems reported, meaning that spins can be re-set on demand by the instrument electronics. As well as being a fundamental achievement in spin physics, this work opens up entirely new research avenues in quantum systems engineering.”

– Dr. Ilya Kuprov, University of Southampton

The Bruker Thesis Prize 2018 lecture “**Magnetic resonance with quantum microwaves**” will be delivered on Monday evening.

Bruker Reception

We are delighted to announce that Bruker Biospin have kindly sponsored a drinks reception on Monday evening to celebrate the Bruker Prize awardees.





Previous winners of the Bruker Lectureship

1986	M. C. R. Symons	1997	K. A. McLauchlan	2008	E. Groenen
1987	K. Möbius	1998	J. R. Pilbrow	2009	G. Jeschke
1988	H. Fischer	1999	J. Schmidt	2010	R. P. Mason
1989	J. S. Hyde	2000	D. Gatteschi	2011	T. Prisner
1990	J. H. Freed	2001	J. Hüttermann	2012	K. M. Salikhov
1991	E. de Boer	2002	G. & S. Eaton (joint)	2013	T. Takui
1992	G. Feher	2003	W. Lubitz	2014	J. Wrachtrup
1993	N. M. Atherton	2004	W. L. Hubbell	2015	R. Bittl
1994	A. Schweiger	2005	K. P. Dinse	2016	R. D. Britt
1995	H. M. McConnell	2006	Y. D. Tsvetkov	2017	P. Höfer
1996	B. M. Hoffman	2007	D. Goldfarb		

Previous winners of the Bruker Thesis Prize

2015	Dr. Joshua Biller, University of Denver
2016	Dr. Claudia Tait, University of Oxford
2017	Dr. Andrin Doll, ETH Zurich





Poster Prizes

IES Poster Prize

The RSC ESR Group Committee is delighted to announce that in total six poster prizes will be awarded to the best poster presentations by young researchers at the 51st Annual International Meeting of the ESR Spectroscopy Group of The Royal Society of Chemistry. All posters presented by young researchers at the conference will be automatically considered for these prizes.

These poster prizes are generously provided by:



The International EPR (ESR) Society (IES) will sponsor two monetary poster prizes. Each prize will also include one year of free IES membership.



Oxford University Press will sponsor two monetary poster prizes.



Springer will provide two poster prizes in the form of generous book vouchers.





RSC ESR Group Committee

Local Organizers

Dr. Maxie Roessler	Queen Mary, University of London
Dr. Enrico Salvadori	Queen Mary, University of London

Scientific Committee

Prof. Eric McInnes (Chair)	University of Manchester
Dr. Ilya Kuprov (Secretary)	University of Southampton
Dr. Fraser MacMillan (Treasurer)	University of East Anglia
Dr. David Norman (Deputy Treasurer)	University of Dundee
Prof. Gunnar Jeschke (international rep.)	ETH Zürich
Dr. Andrew Gibbs (industry rep.)	Bruker UK
Dr. Chris Wedge (Web master)	University of Huddersfield
Dr. Bela Bode	University of St Andrews
Dr. Alice Bowen	University of Oxford
Dr. Emma Richards	University of Cardiff
Prof. Arzhang Ardavan (2017 Organizer)	University of Oxford
Prof. Christiane Timmel (2017 Organizer)	University of Oxford

Organising Team (QMUL)

John Wright	Kaltum Abdiaziz
Martina Cirulli	Wei Song





Practical Information

Registration

Registration for all conference participants will open on Sunday from 16:00 to 18:00 and will take place at the registration desk in the foyer of the Joseph Priestley building. This building will be signposted and can be located on the campus map (page 25). For conference attendees arriving later than this, the registration pack will be available at the Graduate Centre (see a member of the organising team).

Accommodation

Conference attendees staying at the Ibis Budget London Whitechapel Hotel can collect their keys from the hotel after 14:00. Reservations have been made under the name used for conference registration. See <http://www.ibis.com/gb/hotel-8033-ibis-budget-london-white-chapel-brick-lane/index.shtml> for details. Checkout from the hotel must be before 12:00 on the day of departure.

Lectures

All lectures will be held in the Peston lecture theatre in the Graduate Centre (see page 25). Morning sessions start at 9:00 Monday to Thursday. The lecture hall will be signposted.

Information for Speakers

Please allow 5 minutes for discussion at the end of all lectures. Excluding discussion time, plenary lectures will be 35 minutes, invited lectures will be 25 minutes and contributed lectures and JEOL Student Prize talks will be 15 minutes. A data projector, conference computer and laser pointer will be available. Speakers are kindly asked to bring their presentations on a USB stick and upload the presentation onto this computer in the morning before the first session of the day of the presentation. Speakers should ensure their presentations are compatible with the equipment and test them. If it is strictly necessary, speakers may use their own laptops, however we strongly discourage this in order to minimize the turnaround time between lectures. Members of the local organising team will be available to open the lecture theatre and provide limited assistance.

Please would all speakers ensure they keep strictly to the time schedule.

Poster Sessions

Poster sessions will take place on Monday from 16:10 – 17:30 for odd numbered poster boards and on Wednesday from 16:25 – 17:55 for even numbered poster boards. The poster sessions will be held in the foyer of the Graduate Centre, immediately outside the lecture venue. Posters should be set up on Sunday before 18:00 or on Monday morning before the poster session begins. Posters should be removed on Thursday morning. Posters are identified by their number in this booklet. Please affix your poster to the corresponding numbered board only. Material for poster affixing will be provided.

Tea and Coffee Breaks

Tea, coffee and biscuits will be served during the designated morning and afternoon breaks, as well as during the poster sessions.





Meals

All meals during the conference will be served in the Octagon, part of the Queens' Building. The times of meals differ depending on the conference programme of the day and this information can be found in the condensed conference schedule on page 3 of this booklet. For attendees accommodated in the Ibis hotel, a continental breakfast will be provided by the hotel. The barbeque on Sunday evening (18:00 – 20:00) will be held outside the Joseph Priestley building (weather permitting). In the event of rain, participants can take shelter in The Curve, where seating is provided. These locations are indicated on the map (page 25).

Internet Access

WiFi will be available at the Ibis hotel (see the hotel instructions on connectivity). EDUROAM will be available on the QMUL campus. A guest network will also cover participants unable to connect to EDUROAM. Further information will be provided at registration.

Departure

Participants staying in the hotel must vacate their room by 12:00. Lunch will be provided on Thursday after the conference closure. Luggage storage will be provided within the QMUL campus until 15:00 (see announcements for confirmation of the storage location).





Arrival at Queen Mary

Queen Mary University is situated near two underground stations (within 5 minutes walk):

- Mile End (**Central**, **Hammersmith and City**)
- Stepney Green (**Hammersmith and City**, **District**)

Note: Travel on buses and underground services requires an Oyster Card, contactless card or individual ticket purchase. More information can be found here: <https://tfl.gov.uk/fares-and-payments/where-to-top-up-and-buy-tickets>

Travel to Queen Mary University from Ibis Whitechapel

The conference hotel is located in Whitechapel, approximately 1.2 miles from the Queen Mary Mile End campus, and is well linked by public transport:

Bus:

The most direct method of reaching QMUL from the hotel is by bus. The nearest bus stop to the Ibis Whitechapel is at The East London Mosque (3 minutes from the hotel). Direct services QMUL run every 5 minutes.

Service	Start	Finish
205 (Bow Church)	The East London Mosque	Queen Mary/University of London
25 (Ilford)	The East London Mosque	Queen Mary/University of London

Underground:

The underground service can also be used. Whitechapel underground station is approximately 6 minutes from the hotel. Services from this station run every 5 minutes.

Service	Start	Finish
Hammersmith and City (East-bound)	Whitechapel	Stepney Green
District (East-bound)	Whitechapel	Stepney Green

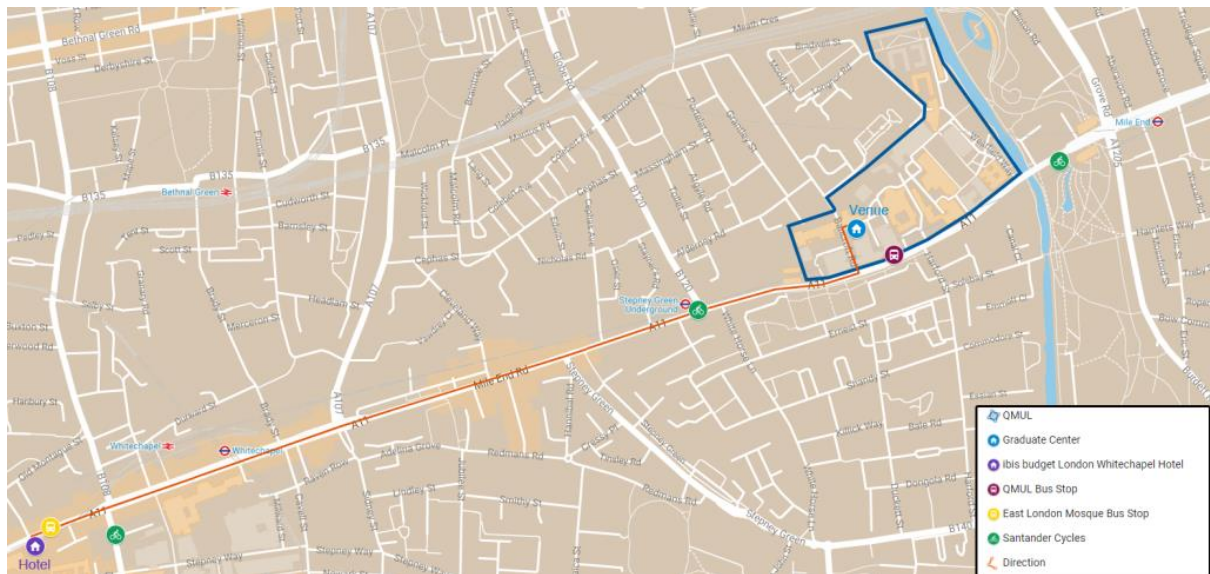
Walking and Santander Cycles

QMUL is only a 30-minute walk from the Ibis Whitechapel. There is a Santander Cycle docking station located on New Road, which intersects Whitechapel road near the Ibis hotel. There are Santander Cycle docking stations near Stepney Green and Mile End Stations. Pay as you go costs £2 for 24-hour access plus any extra ride charges for journeys over 30 minutes. More information about Santander cycles can be found at <https://tfl.gov.uk/modes/cycling/santander-cycles>.



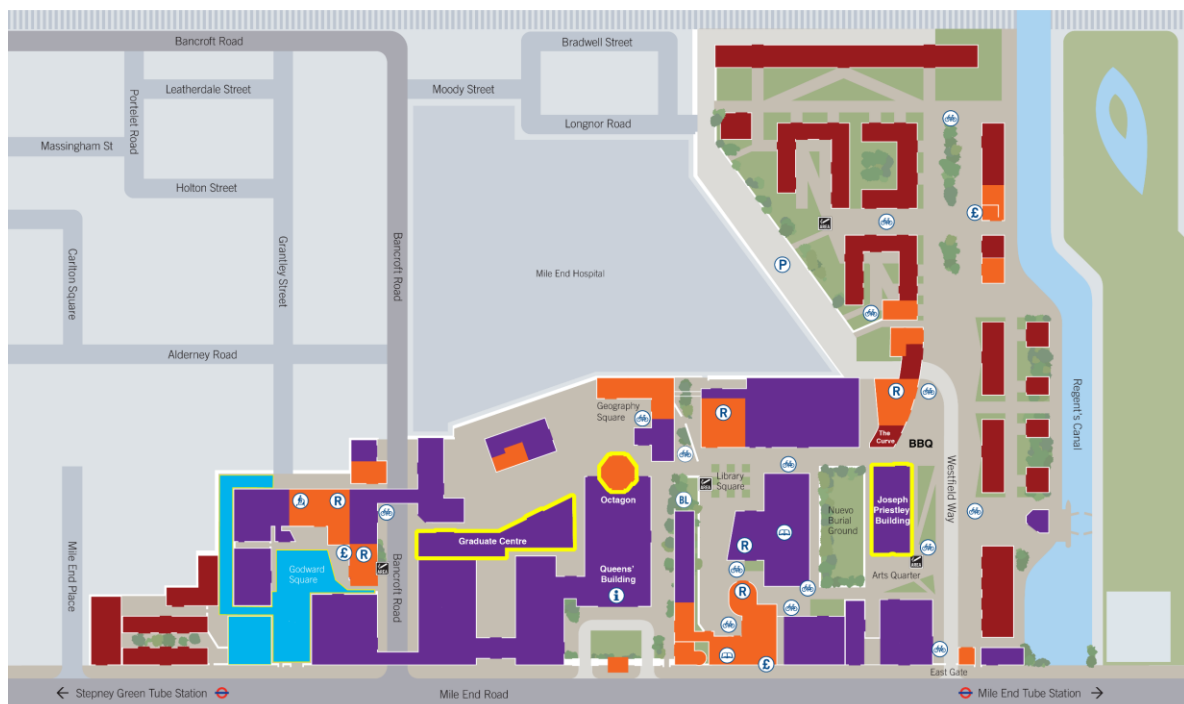


Map of Route from Hotel to QMUL



Map of QMUL Campus

Conference venues are highlighted in yellow





Location and Historical Notes

Queen Mary University of London (QMUL) is an integral part of the East End of London. QMUL was founded in the mid-Victorian era by a philanthropic organisation known as The People's Palace devoted to bringing culture, recreation and education to the people London's East End. The university evolved around The People's Palace, the central clock-tower building on the Mile End Campus.

Besides a calendar of social events and facilities, the People's Palace also established Technical Schools to train a new generation of tradespeople for the key industries of east London. As the success of the People's Palace Technical Schools grew, it was decided that teaching would be extended in the sciences and introduced in the arts and humanities. Awarded its own Royal Charter by Queen Mary of Teck, the institution originally took the name Queen Mary College. In the



latter half of the 20th century it merged with Westfield College, an early pioneer of women's education, and St Bartholomew's and the Royal London School of Medicine and Dentistry.

Today, teaching and research at Queen Mary University of London spans three faculties: Humanities and Social Sciences; Science and Engineering; and Barts and The London School of Medicine and Dentistry. The main campus is in Mile End (East London) with other campuses in Holborn, Smithfield and Whitechapel.

QMUL is a Russell Group university and hosts an international community, which includes 23,120 students in total (16,993 undergraduates and 4,842 postgraduates) from 162 nations around the globe. A further group of 3,400 students undertake joint programmes overseas in China (Nanchang and Beijing), Greece (Pireaus) and France (Paris).

Chemistry at Queen Mary College dates back to 1887 while chemistry at Westfield College was founded in 1960. In 1984, before the QMC-Westfield merger, chemistry staff at Westfield (and three from Chelsea College) joined colleagues at QMC at the Mile End campus. In 2006, the Department of Chemistry merged with the School of Biological Sciences to form the School of Biological and Chemical Sciences at QMUL.

Conference Venue

The conference will be held on the Mile End campus, in the historical Queen's Building (pictured above) and the brand-new Graduate Centre.





The Graduate Centre



Conference talks, coffee breaks and poster sessions will be held at the graduate Centre. The 200-seat Peston lecture theatre enjoys natural light and the foyer (that includes a Starbucks café) provides an open space for discussion. Completed in 2016, the seven-story building includes 7,700 square metres of new learning and teaching space. The spaces and working areas of the Graduate Centre were specifically designed bearing in mind the needs and working patterns of QMUL postgraduates. In addition, it is the home for the School of Economics and Finance, the Doctoral College and the Research Degrees Office. The top floor offers a panoramic terrace with magnificent views of Canary Wharf and The City of London.

The Octagon



The conference banquet, lunches and dinners will be hosted in the Octagon (pictured above), part of the Grade II listed Queen's Building. Formerly the library, the Octagon was built in 1887 and designed by Victorian architect ER Robson who was inspired by the Reading Room at the British Museum. In 2006, the room was fully restored and brightly coloured leather bound books have been reinstated to the bookshelves with busts of famous literati looking down from the high domed ceiling, creating an atmospheric setting.



Electron Paramagnetic Resonance spectroscopy at Queen Mary University of London

Electron Paramagnetic Resonance Spectroscopy has a long and rich history at Queen Mary University of London. EPR commenced in the late 1970's, at what was then Queen Mary College, University of London (QMC). A Bruker 200D X-band spectrometer was purchased for an Intercollegiate Research Service based in the Chemistry department, funded by the University of London. Keith Sales was the member of academic staff supervising the service, which was operated by Dr Duro Odowole. There was a steady stream of publications acknowledging the use of this facility up until the late 1990's. The main research topic was the dating of archaeological samples using the ESR signal resulting from gamma radiation, although other systems were also studied. Dr Chris Rhodes was another EPR spectroscopist appointed as a member of staff in the department of Chemistry in 1989, who was then promoted to a research professor position at Liverpool John Moores University in 1994.

Peter Heathcote moved to the School of Biological Sciences at QMC in 1984, using electron paramagnetic resonance spectroscopy to investigate electron transfer and protein cofactor interactions in photosynthetic reaction centres. Steve Rigby, who brought with him an expertise in Electron Nuclear Double Resonance (ENDOR) Spectroscopy, joined him in 1995. Both Peter and Steve used EPR facilities at University College London (in collaboration with Professor Mike Evans) and King's College London (with Professor Richard Cammack). In 2001 they were successful in obtaining funding from the Science Research Infrastructure fund to purchase a Bruker Eleksys E500 X-band continuous wave (CW) spectrometer, which was subsequently upgraded to an E580 pulsed EPR spectrometer operating at X and Q-band. The research using these facilities expanded into studies of respiratory chain complexes (with Professor Peter Rich at UCL) and enzymes and intermediates in tetrapyrrole biosynthesis (with Professor Martin Warren who had joined QMUL).



Steve Rigby moved to become a Reader at the University of Manchester in 2009. Dr. Maxie Roessler was appointed as a Lecturer in Chemistry and Biochemistry in the School of Biological and Chemical Sciences in 2013, with a research background in EPR spectroscopy applied to large metalloenzymes such as hydrogenases and respiratory complex I. In 2015 Dr. Enrico Salvadori was appointed as the EPR Facility Research Fellow and brought an expertise on photoexcited transient species ranging from photosynthesis to materials science. The X-Q-band spectrometer now features a close-cycle cryostat (Cryogenic) and a tunable OPO laser enables photo excitation in situ and Maxie and Enrico are committed to developing the EPR facility at QMUL into a cross-faculty research centre spanning chemistry, biochemistry and materials science.

The local organisers thank Prof. Peter Heathcote for these historical notes





Social Programme

Free Afternoon on Tuesday

With its 27 million visitors every year, London is the most visited city in Europe. The free afternoon will give the participants the opportunity to explore the city that is home to world-class museums, beautiful parks, buzzing markets and stunning viewpoints. The free afternoon allows plenty of time to explore what London has to offer and below are a few recommendations

One of London's main attraction is its sensational selection of **museums and galleries**. Among these, the British Museum and the National Gallery offer amazing collections of rare and historic artefacts from around the world, with highlights including the Rosetta Stone and the Bathers at Asnieres by Seurat, respectively. The Tate Modern is also noteworthy, where the amazing work of modern artists such as Cezanne, Picasso, Dali and Warhol are housed in the former Bankside Power Station on the Thames river. For those who cannot handle a science-free afternoon, the Science Museum offers interactive galleries that bring to life first scientific principles and contemporary science debates. Permanent collections are free, whereas tickets for seasonal exhibitions (as well as opening times and directions) can be found on the museums respective websites.



If you feel overwhelmed with the chaotic Londoner life, you may well choose to enjoy your free afternoon in one of the many **beautiful parks** London can offer. Centrally located parks such as Hyde Park, Regent's Park and St James's Park offer the opportunity to take a walk among roses gardens and huge lakes but if you are looking for a pastoral landscape with ancient trees, plants and animals you should pay a visit to the Richmond Park. The Victoria Park is also a great alternative if you wish to remain close to the conference venue.

London markets are ideal shopping destinations, whether you are looking for a special gift to bring back home or some vintage clothes or just a quick bite on the go. The classy Covent Garden, the Old Spitafields Market and the famous-punk Camden Lock Market are open seven days per week until 18:00 but if you are looking for an around-the-world foodie experience the Borough Market and the Broadway Market (open only on Saturdays) will definitely satisfy your cravings.





If you want to see the entire city of London in just one afternoon the best thing to do is head upwards and look down on the city's many famous buildings and attractions. You can get a ticket for around £30 to go up the Shard or choose the more classic London Eye (price around £25) where the view of Westminster and St Paul's area is pretty good from all angles. You can also get an amazing viewpoint experience for free, either from the Primrose Hill or from the Sky Garden building – just remember to book the entrance ticket well in advance. Another cheap alternative is the Emirates Air Line, a cable car that crosses the River Thames – around the same area where the O2 is – at only £3.30 for Oyster card holders.

For those wishing to explore a more historical side of the city, a tour including the Tower of London, Westminster Abbey and St Paul's Cathedral is highly recommended. Tickets for these attractions can be bought online and discounts for students are also available. If you are fond of royal palaces – and of the Royal Family – then Buckingham Palace is also worth a visit (but only from the outside during the conference time!).



Last (but not least) you can go to King's Cross Station. Push a trolley through to Harry Potter's magical world at the wall marked Platform 9³/₄ and step inside the magical shop. You can find all the Hogwarts merchandise a devoted fan could ever want.

JEOL Reception

We are delighted to announce that JEOL have kindly sponsored a drinks reception to celebrate the 21st Annual JEOL Prize Talk Competition.



Bruker Reception

We are delighted to announce that Bruker Biospin have kindly sponsored a drinks reception to celebrate the Bruker Prize award-ees.





Conference Banquet

The culmination of the week's social activities will be the conference banquet in the Octagon on Wednesday evening.

Accompanying Persons

Although there is no formal program of events for accompanying persons, there are numerous interesting places to visit both within London and the surrounding area, most of which are easily accessible via public transport. Useful tourist information on free attractions can be found on the [timeout London](#), [lonely planet](#), and [visit London](#) websites.





University of Glasgow

**52nd Annual International Meeting of the
ESR Spectroscopy Group of the
Royal Society of Chemistry**

Sunday 7th to Thursday 11th April 2019



Talk Abstracts

Ultra-Sensitive Operando Detection of Paramagnetic States in Silicon Solar Cells

J. Möser¹, S. Künstner¹, A. Schnegg¹, J. Behrends², J. Anders³, **K. Lips**^{1,2}

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² Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, Germany ³ Institute of Smart Sensors, Universität of Stuttgart, Germany e-mail: lips@helmholtz-berlin.de

Almost 90% of all installed photovoltaic (PV) modules are fabricated using wafer-based and thin-film silicon technology. The technology has reached a mature stage and current generation costs of clearly below 0.1US\$/kWh are reached. Further cost reduction can only be achieved by further increasing module efficiency. The current efficiency record for silicon solar cells is 26.6 % and was made possible due to excellent passivation and electrical properties of the only 3-10 nm thin amorphous silicon (a-Si:H) layer that forms a charge selective heterocontact with the crystalline silicon (c-Si) absorber. This then replaces the classical silicon homo-pn junction that is achieved through phosphorus and boron doping of c-Si. Despite the enormous success of this silicon heterojunction solar cell, many open questions remain about the stability as well as the nature of the defect states of the thin a-Si:H contact layer. Most of these defects are paramagnetic and are induced by compositional and material disorder. These paramagnetic defects act as charge-carrier traps and recombination centers. However, fully processed high efficiency PV devices with complex morphologies typically do not exhibit enough paramagnetic states to be observed by EPR. However, due to the weak spin-orbit coupling in silicon these defects can induce spin-dependent charge carrier transport and recombination which can be detected with many orders of magnitude higher sensitivity than EPR in pulsed and cw electrically detected magnetic resonance experiments (pEDMR and cwEDMR, respectively).

After reviewing the status of PV technology, we will introduce the EDMR technique and present data that clearly reveals the participation of paramagnetic species (defects, triplet excitons etc.) in transport and recombination processes in thin silicon heterostructure solar cells. Structural information obtained from pulsed multi-frequency EPR and transient EPR on powder samples is complemented by cw and pEDMR ranging from X-band up to 263 GHz. Benefiting from the increased resolution of multi-frequency pEDMR and the possibility to coherently manipulate coupled spins by pulsed EDMR excitation schemes, a complete picture of charge carrier transport and recombination in silicon materials and solar cells is achieved showing that transport and recombination is governed by a three-particle process. An outlook to fascinating new applications of pEDMR using EPR-on-a-chip concepts will be also given.

The path to enlightenment: What TREPR teaches us about electronic structure, morphology, and flexibility of conjugated polymers

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² *Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 31, 79104 Freiburg, Germany*

³ *Current address: Professur Polymerchemie, TU Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany*

Illuminating conjugated polymers not only leads to excited states, but sheds light on some of the most important aspects of device efficiency in organic electronics as well. The interplay between electronic structure, morphology, flexibility, and local ordering, while at the heart of structure-function relationship of organic electronic materials, is still barely understood. Time-resolved EPR (TREPR) spectroscopy has proven valuable to gain further insight.

Previously, we established TREPR for probing both the orientation and degree of ordering of polymers [1], nicely complementing other methods for structure determination. In another study, we revealed the origin of triplet states, bringing a seemingly forgotten route back into focus: spin-forbidden direct $S_0 \rightarrow T$ excitation, with potential high impact for device efficiency [2].

Here, we demonstrate the power of TREPR, combined with DFT calculations, to discriminate between electronic structure and planarity when it comes to determining factors for exciton delocalisation. In a systematic approach, a series of building blocks of PNDIT2 as well as the polymer with two chain lengths have been studied. Surprisingly, the triplet exciton on PNDIT2 is highly localised, spanning no more than two repeat units, rendering the building block NDI-T2-NDI a perfect model for the polymer [3].

Additionally, we show the intrinsically high sensitivity of TREPR to the local environment of the exciton to make it an excellent tool for investigating polymer morphology. The parameters readily available from spectral simulations allow us to probe the available conformational subspace of the polymer backbone and thus the degree of order even in solution. PNDIT2 shows striking differences in different solvents, 1-chloronaphthalene and toluene, that can be attributed to the formation of locally highly ordered domains if dissolved in toluene. Additionally, different modes of exciton delocalisation, namely intra- and interchain, dominate depending on the solvent, the latter resembling the situation in thin film [4].

[1] T. Biskup, M. Sommer S. Rein, D. L. Meyer, M. Kohlstädt, U. Würfel, S. Weber, *Angew. Chem. Int. Ed.*, **2015**, 54, 7707–7710

[2] D. L. Meyer, F. Lombeck, S. Huettner, M. Sommer, T. Biskup, *J. Phys. Chem. Lett.*, **2017**, 8, 1677–1682

[3] D. L. Meyer, R. Matsidik, M. Sommer, T. Biskup, *Phys. Chem. Chem. Phys.*, **2018**, 20, 2716–2723

[4] D. L. Meyer, R. Matsidik, S. Huettner, M. Sommer, T. Biskup, *Adv. Electron. Mater.*, **2018**, 4, 1700385

EPR studies on the photoinduced electron-transfer in viologens-tetraarylborate complexes

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² Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403 USA

Building upon our recent studies of photoinduced charge shifts and electron transfer in a viologen-tetraphenylborate complex, herein, we extend our investigation to characterize and examine the light induced electron transfer of a series of viologen-derivatives/tetraarylborate complexes by EPR spectroscopy [1]. Ion-pair complexes of substituted tetraarylborate ions with methyl- or benzyl- viologen were prepared, characterized and its photophysical and photochemical properties studied by steady-state spectroscopic methods. Photoinduced electron transfer from the tetraarylborate anion to the viologen dication, as consequence of a push-pull character of the ion-pair complex triplet-state to yielding viologen cation radical and the borate radical, was identified by EPR spectroscopy. Interestingly, the lifetime decay of the formed viologen cation radical decreases linearly with the increasing continuous-wave microwave power (Figure 1). Indeed, an external continuous-wave microwave field may induce magneto-dipole transitions in the viologen radical, promoting an additional mixing between the excited energy states of the viologen conformer's, if the microwave field frequency is in resonance with the corresponding EPR transition. Such additional mixing of the energy states creates additional changes of the excited state dynamics.

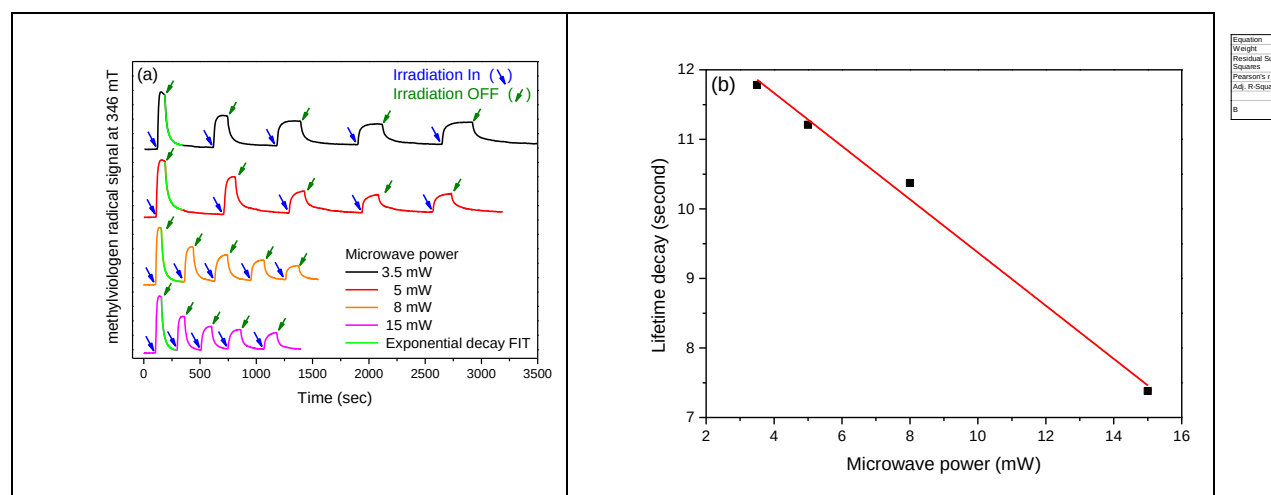


Figure. (a) Time-sweep EPR signal recorded in the presence (In) and absence (OFF) of light ($\lambda_{\text{exc}} = 410 \text{ nm}$) irradiation of a powder sample of $\text{MV}^{2+}2\text{B}(\text{Ph})_4^-$. (b) Linear dependence between viologen radical lifetime and the CW microwave power. The viologen radical lifetime was obtained by fitting an exponential decay function for the first in/off light cycle (green line). Complex: methyl-viologen:tetraphenylborate ($\text{MV}^{2+}2\text{B}(\text{Ph})_4^-$).

[1] W. G. Santos, D. S. Budkina, V. M. Deflon, A. N. Tarnovsky, D. R. Cardoso, M. D. E. Forbes, *J. Am. Chem. Soc.*, **2017**, 139, 7681-7684.

Molecular Design and Synthesis as a Vector for Understanding Electron Spin Relaxation

D. E. Freedman¹, M. S. Fataftah¹, J. M. Zadrozny², M. J. Graham,¹ C.-J. Yu,¹

¹ Department of Chemistry, Northwestern University, Evanston, Illinois 60208 USA

² Colorado State University, Fort Collins, Colorado 80523 USA

Our approach to the challenge of creating and understanding qubits, the smallest unit of a quantum computer focuses on harnessing coordination to rationally design new molecules and materials. Here, we suggest that the inherent synthetic tunability accessible with coordination chemistry and supramolecular chemistry will enable the rational design of molecular qubits which can be designed to approach any specific qubit application. Within this framework, we are working on (a) creating design principles to understand the fundamental contributions to electronic spin coherence; (b) employing those newfound principles to create long-lived qubits; (c) incorporating qubits into larger architectures. Magnetic molecules offer tremendous potential as hosts for electron spin-based qubits. Electron spins in magnetic molecules offer three advantages over solid-state systems: reproducible fabrication of qubits via chemical synthesis, extraordinary tunability of the spins by chemical design, and ability of the qubit monomers to form large-scale ordered arrays through assembly reactions or the creation of framework materials. Studies towards these goals will be discussed

[1] Graham, M. J.; Yu, C.; Krzyaniak, M.; Wasielewski, M. R.; Freedman, D. E. *J. Am. Chem. Soc.* **2017**, *139*, 3196–3201.

[2] Graham, M. J.; Zadrozny, J. M.; Fataftah, M. S.; Freedman, D. E. *Chem. Mater.* **2017**, *29*, 1885–1897.

[3] Zadrozny, J. M.; Gallagher, A. T.; Harris, T. D.; Freedman, D. E. *J. Am. Chem. Soc.* **2017**, *139*, 7089–7094.

ESR Spectroscopy: Monoradical and Biradical as building block for magnetic Graphene Nanoribbon

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Achieving long spin relaxation times and phase coherence lengths is one of the main challenges encountered in modern physics and chemistry. Superposition and entanglement of quantum states are two fundamental ingredients for those materials called to face this challenge and being implemented in new generation computers. Single-Magnet Molecules based on rare-earth metal have played a central role in the last decades in this portrait. Nevertheless, despite of the recent results displaying a magnetic bistability at 60K temperatures¹, single-molecule magnets contain a vast number of either expensive transition metal or (even more high-priced) lanthanide ions, that have to be carefully engineered with ligand environment, with not so few difficulties.

On the other hand, the discovery of long relaxation times (~ 2 ns) and coherence lengths (~ 0.7 μ m) in bilayer graphene² have increased the confidence in their use as materials for spintronics and quantum computer devices. In this picture, graphene nanoribbon (GNRs) would be a more suitable candidate for these type of materials. Furthermore, magnetic edges in graphene nanoribbons have been supported by an intense theoretical study³ because their coherent manipulation would be a milestone for spintronic and quantum computing applications. Here we report a complete pulse and laser ESR investigations of a mono and biradical compounds, which their structure can be used as building block for a MGNRs. It has been shown that the echo phase memory time T_M and the rate of quantum dissipation (related to the more familiar parameter T_1) are promising comparable with the molecular magnets performance. Information on the radical environment are indirectly extracted both in ground electronic and in excited states thanks to the laser excitations during pulse sequences and to the correlation between the electron spins and their surroundings.

[1] R. Layfield, *Angew. Chem. Int. Ed.*, **2017**, 56, 11445–11449

[2] W. Han, *Phys. Rev. Lett.*, **2011**, 107, 047206–047210.

[3] M.S. Dresselhaus, *Review of Modern Physics*, 2016, Vol. 88, No. 2.

Magnetic Nanoparticles in Bioreactors: host-guest characterization by EPR and Mössbauer Spectroscopies

M. Fittipaldi¹, A. Cini¹, R. Mercatelli¹, E. Falvo³, P. Ceci³, D. Gatteschi², M. Ardini⁴, B.D. Howes², A. Ilari³, A. Fiorillo³, G. Spina¹, S. Stefanini³

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³ Istituto di Biologia e Patologia Molecolari, Consiglio Nazionale delle Ricerche, P.le Aldo Moro 7, 00185 Roma, Italy

⁴ Dipartimento di Scienze Biochimiche, Università "Sapienza", P.le Aldo Moro 5, 00185 Roma, Italy

We have investigated Magnetic Nanoparticles (MNPs) of spinel type iron oxide (of approximately 8 and 4 nm) mineralized in the internal cavity of the bioreactor ferritin-like nanocage. In particular, we have used Electron Magnetic Resonance (EMR) spectroscopy and taken advantage of the capacity of the protein shells to control the size of the MNPs. EMR measurements in perpendicular and parallel configurations have been recorded at various temperatures. An approach based on the giant spin is used to interpret the experimental results. The analysis indicates that the observed quantum behaviour has to be ascribed to the whole MNP and that the thermal population of excited spin states has a strong influence on the EMR behavior of MNPs.[1,2]

The host reactors (ferritin) contain 24 ferroxidase centers, where the mineralization initiates, each constituted by two metal binding sites. These sites in human H ferritin have been characterized by a combination of Mössbauer and EPR experiments that have shown both Fe(II) and Mn(II) ions are able to bind the ferroxidase centre forming a Fe-Mn cofactor. Moreover, it is demonstrated that Mn influences the Fe binding and has a positive impact on protein function, improving the efficiency of the ferroxidation reaction.[3]

[1] M. Fittipaldi, R. Mercatelli, S. Sottini, P. Ceci, E. Falvo, D. Gatteschi, *Phys. Chem. Chem. Phys.*, **2016**, 8(5): 3591-3597

[2] A. Cini, P. Ceci, E. Falvo, D. Gatteschi, M. Fittipaldi, *Z. Phys. Chem.*, **2017**, 231(4):745–757

[3] M. Ardini, B. D. Howes, A. Fiorillo, E. Falvo, S. Sottini, D. Rovai, M. Lantieri, A. Ilari, D. Gatteschi, G. Spina, E. Chiancone, S. Stefanini, M. Fittipaldi, *J. Inorg. Biochem.*, **2018**, 103–112

Endohedral Fullerenes as Molecular Qubits

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Quantum computation could outperform classical approaches in cryptography and database searching. Among various quantum bits (qubits) candidates, molecular nanomagnets are found to be prominent since their collective spins are tunable as required. However, the nuclear spins from the ligand can act as a source of Overhauser field to decoher the electron spins. Here we demonstrate that by encapsulating the electron spins in fullerenes, it is possible to elongate the quantum coherence time largely even for the anisotropic high spin systems with many nuclear spins. The rotation of the inner group of the endohedral fullerene ($\text{Sc}_3\text{C}_2@\text{C}_{80}$) can lead to a crossover of the quantum coherence behavior [1]. The anisotropic high spin system ($\text{Gd}_2@\text{C}_{79}\text{N}$) affords diverse Rabi cycles, allowing arbitrary superposition state manipulation between each adjacent level [2]. Our research suggests that this molecular magnetic material of anisotropic high spin fulfills the requirement for implementing Grover's algorithm.

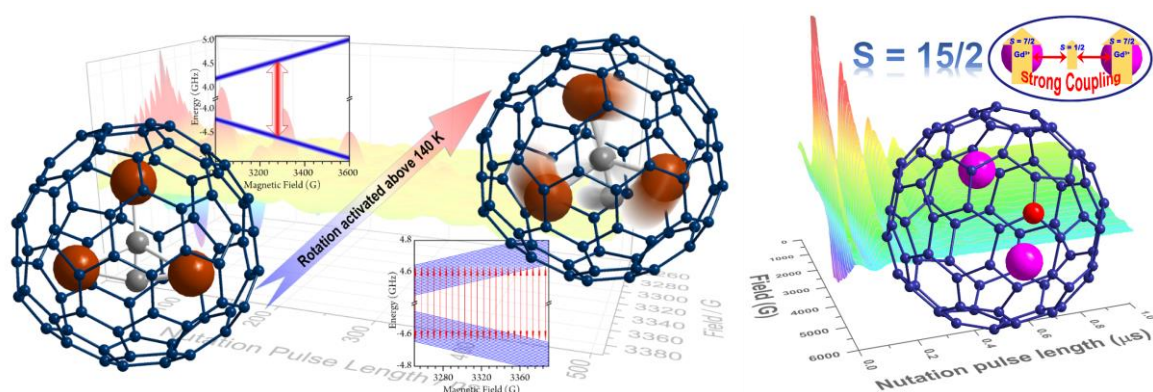


Figure 1 Endohedral fullerenes ($\text{Sc}_3\text{C}_2@\text{C}_{80}$) and ($\text{Gd}_2@\text{C}_{79}\text{N}$) are good candidates for molecular spin qubits.

[1] Z. Liu, C. Wang*, S. D. Jiang*, S. Gao* *Chem. Sci.*, **2018**, 9, 457-462.

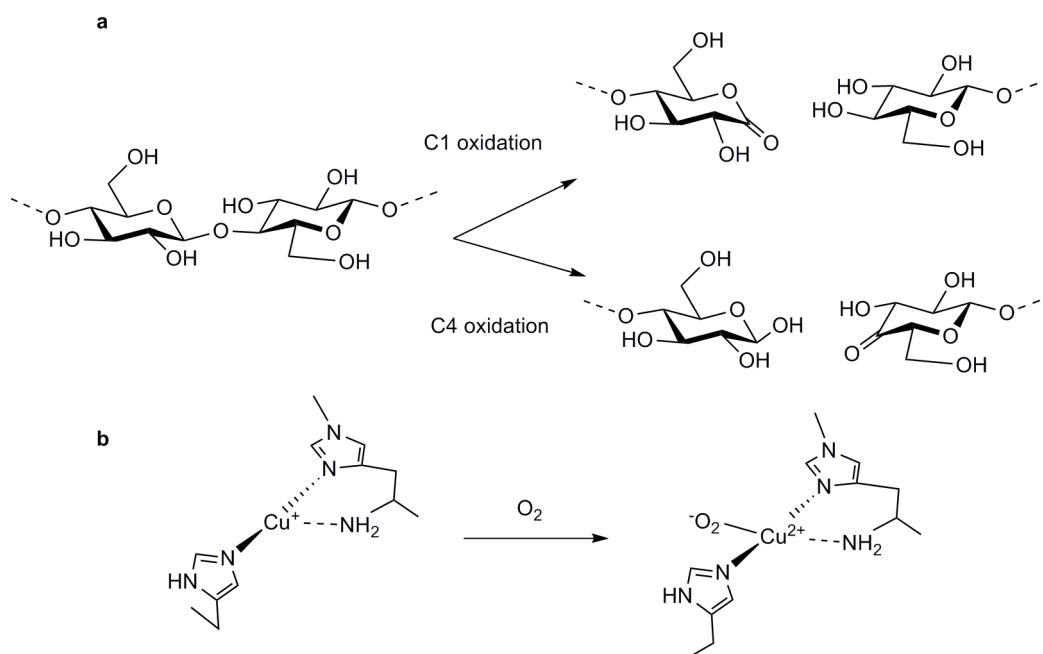
[2] Z. Q. Hu, B. W. Dong, Z. Shi*, S. D. Jiang*, S. Gao* *J. Am. Chem. Soc.*, **2018**, 140, 1123-1130.

Multi-frequency EPR spectroscopy and Angular Overlap Model Analysis of the Copper Active Site of *Lytic Polysaccharide Monooxygenases*

P. H. Walton¹, L. Ciano¹

¹ Department of Chemistry, University of York, Heslington, York, UK, YO10 5DD

Lytic polysaccharide monooxygenases (LPMOs) are copper-containing enzymes that oxidatively cleave polysaccharides such as cellulose, Figure 1a [1]. LPMOs have an active site which contains a single Cu ion within a coordination environment known as the histidine brace at which oxygen binds to the copper (Figure 1b). We have carried out extensive structural, EPR spectroscopic and theoretical studies on the active site [2] revealing significant electronic changes at the copper when the enzyme binds to its natural substrate. These changes have been examined using in-house software based on the Angular Overlap Model, which illustrates how semi-empirical methods can be effectively used to gain electronic insight from spectroscopic data, including that gained from EPR spectroscopy.



[1] J. Quinlan et al, *Proc. Nat. Acad. Sci.*, **2011**, 37, 15079–15084.

[2] K. E. H. Frandsen et al, *Nature Chem. Biol.*, **2016**, 12(4), 298–303.

H₂O₂ activation of the dye-decolorizing peroxidase DtpA from *Streptomyces lividans* – is it one Compound I or two of them?

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DtpA is one of the recently discovered dye-decolorizing peroxidases from the soil dwelling bacterium *Streptomyces lividans* [1]. The family of the dye-decolorizing peroxidases is in the focus of the researchers' interest in developing several biotechnology applications linked to the demonstrated *in vitro* ability of the enzymes to degrade lignin as well as anthraquinone-type dyes used in textile industry. Whilst the *in vivo* substrates are not known, the *in vitro* reactivity towards large size molecules indicates that their binding site cannot be close to the haem, where H₂O₂ comes to play, but should rather be somewhere on the enzyme's surface. This means there should be an electron transfer pathway [2] between the surface and the haem site. The transfer starts at the haem area where an electron is moved from the porphyrin to H₂O₂ forming a Compound I (Figure 1, A, B). This is followed by Compound I reduction by an electron transferred from a site on the enzyme - with a concomitant formation of a free radical on that site (Figure 1, B, C). We report here a new version of TRSSA (Tyrosyl Radical Spectra Simulation Algorithm [3]) that has been used to assign the radical location to Tyr374.

Since the assignment to this particular tyrosine residue (of the three present in the DtpA structure) had an ambiguity element due to the similarity in the ring rotational conformations in all three tyrosines, we performed the site directed mutagenesis study that has confirmed that only the replacement of the Tyr374 residue has a dramatic effect on the free radical formed under H₂O₂ treatment. For the first time in the peroxidases activation studies, we report detection of two forms of Compound I, with slightly differing EPR parameters. While this finding needs justification and further investigation, if shown to be systematic and clearly linked to yet to be identified reaction conditions, it will reveal a new mechanistic feature of peroxidases that might have implications to our understanding and manipulating of the biotechnologically relevant mechanisms and kinetics.

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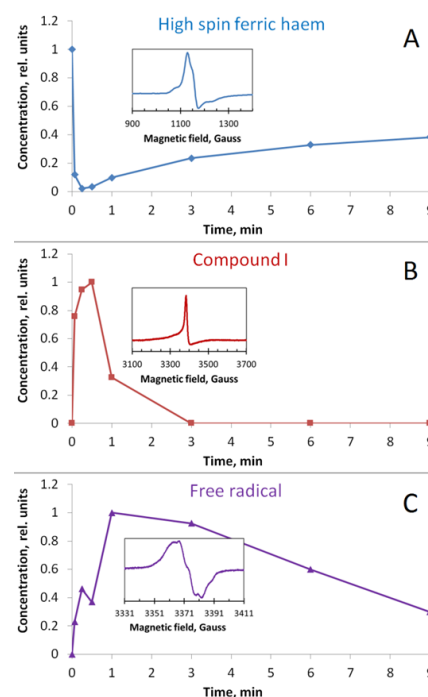


Figure 1. The kinetic dependences of the Fe³⁺ haem state, the species assigned to Compound I and the free radical assigned to Tyr374 in 40 μ M DtpA activated by 400 μ M H₂O₂.

Small dsDNA as model systems for orientation selective pulsed EPR

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In the study of small and rigid biomolecules, EPR pulsed dipolar spectroscopy (PDS) methods can provide unique and exciting insights into structure, structural distributions and dynamics. For nitroxides, anisotropy of the electron-Zeeman interaction, resolved at high field, and anisotropic hyperfine interactions to the nitrogen, allow PDS data to be measured, which encodes the relative orientation of two nitroxid spin labels with respect to each other. Careful analysis of such data can be used for structural distribution studies, from which information about the flexibility of the system can be inferred [1].

Direct interpretation of the orientation-selective PDS data can be ambiguous and challenging. For this reason it is preferable to evaluate the experimental data relative to a biologically acceptable model; this increases the likelihood of determining a reasonable and unique solution.

Small double-stranded DNA (dsDNA) with the rigid ζ spin label is a biological system well suited for such studies, as it has been shown to give highly orientation selective PDS data. This data has been used as a sensitive benchmark for the evaluation of new MD simulation techniques for nucleic acids [2]. MD simulations provided a distribution of nucleic acid structures to which spin-labels were added, and orientation selective Pulsed Electron Double Resonance (PELDOR) data calculated for the resulting ensemble. Comparison of these calculated data sets to experimental data showed that new force fields demonstrate a significant improvement in the agreement between the simulated and experimental PSD data and therefore the structural distributions frozen into the EPR samples.

Understanding the structural conformers of the dsDNA has allowed these systems to be used as biological model systems. One application is the evaluation of simulation procedures for 2D-SIFTER (Single Frequency Technique for Refocusing Dipolar Couplings) [3]. This broadband excitation pulse technique enables the collection of the orientation selective data by direct Fourier transform. Such experiments have the potential to offer improved S/N and resolution for the determination of the angular information between two rigidly attached nitroxides.

Additionally, room temperature (RT) PELDOR measurements on these DNA sequences show striking differences to measurements recorded at cryogenic temperatures. This can be attributed to motional averaging of the fast dynamic modes in the nanosecond range at RT, and can be corroborated by MD calculations.

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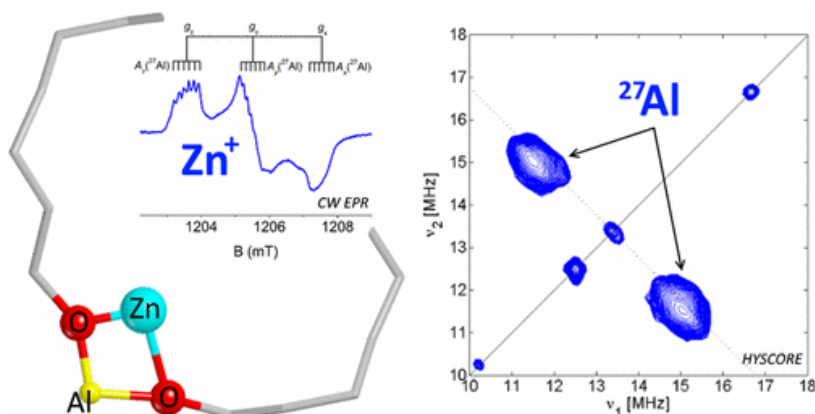
The Unusual Chemistry of Group XII Elements in Zeolites. An Electron Magnetic Resonance Investigation.

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In this work, the formation and stabilization of group-12 unusual univalent species (Zn^+ , Cd^+) in the cavities and channels of zeolites is demonstrated and investigated by means of advanced Electron Paramagnetic Resonance (EPR) spectroscopy. The intense electrostatic fields within zeolite networks provide the driving force for the spontaneous ionization of molecular species and metal atoms and allow for the stabilization of uncommon formal valence states, resulting in unique physical and chemical properties.[1,2] Unlike mercury, which has an extensive monovalent oxidation state chemistry, zinc and cadmium usually adopts the +2 oxidation state while the +1 oxidation state is very unusual. Zn^+ [3] and Cd^+ are paramagnetic ions with $nd^{10} (n+1)s^1$ electronic configuration, therefore, Electron Paramagnetic Resonance (EPR) spectroscopy is uniquely informative in the study of these chemical species.

Modern pulse EPR techniques reveal that Zn^+ and Cd^+ species are formed at specific sites of the zeolite, and allow resolving the electronic and geometric structure at the molecular level. Advanced pulse EPR techniques allow mapping the spin-density distribution over framework magnetic nuclei (^{27}Al) providing detailed description of the stabilizing site. The results are consistent with metal ions being stabilized at the Si-OH-Al bridges, replacing for Brønsted acidic proton sites. The chemical accessibility and reactivity of the metal species are preliminary tested by using different probe molecules (e.g. O_2 , NH_3 , C_2H_4), suggesting potential applications in catalytic processes.



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It's not just $1/r^6$: magnetic anisotropy effects on lanthanide induced paramagnetic relaxation enhancement

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Lanthanide ions accelerate nuclear spin relaxation by two primary mechanisms: dipolar and Curie. Both are commonly assumed to depend on the length of the lanthanide-nucleus vector, but not on its direction. Here we demonstrate that *this is wrong* – careful proton relaxation data analysis in a series of isostructural lanthanide complexes (Ln=Tb, Dy, Ho, Er, Tm, Yb) reveals angular dependence in both Curie and dipolar relaxation. The reasons are:

- that magnetic susceptibility anisotropy can be of the same order of magnitude as the isotropic part (contradicting the unstated assumption in Gueron's theory of the Curie relaxation process [1]);
- that zero-field splitting can be much stronger than the electron Zeeman interaction (Bloembergen's original theory of the lanthanide-induced dipolar relaxation process makes the opposite assumption [2]).

These factors go beyond cross-correlation effects; they alter the relaxation theory treatment and make angular dependencies appear in the nuclear spin relaxation rates.

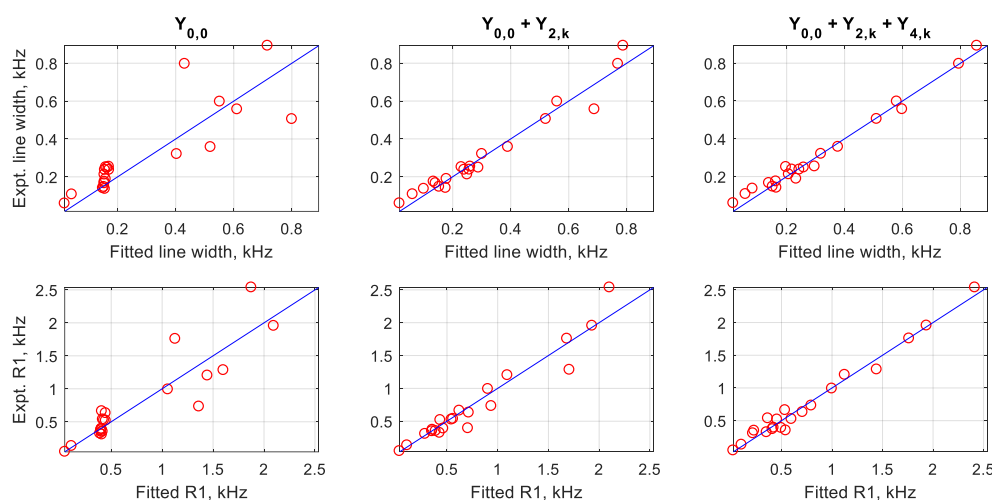


Figure 1. A demonstration that 2nd and 4th rank anisotropy is clearly present in the proton relaxation data of a Tb(III) complex with a derivative of 1,4,7,10-tetraazacyclododecane. **Left:** fits to the isotropic expressions commonly used in the biological literature. **Middle:** fits to expressions augmented with 2nd rank spherical harmonics of the electron-nuclear direction. **Right:** fits to the expressions augmented with 2nd and 4th rank spherical harmonics of the electron-nuclear direction.

Those angular dependencies are impossible to ignore (Figure 1) – we demonstrate this both theoretically and experimentally, and suggest that a major revision is needed of the way lanthanide-induced relaxation data is used in structural biology.

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Magnetic resonance with quantum microwaves

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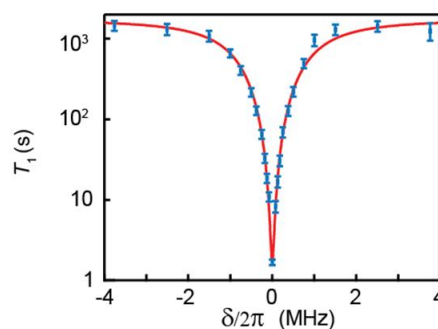
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In electron-spin resonance (ESR) experiments, the quantum nature of the microwave fields emitted by the spins during their Larmor precession is usually neglected. Using a Josephson parametric microwave amplifier and a small mode volume super-conducting microwave ESR resonator, we first demonstrate the operation of an ESR spectrometer where the detection sensitivity is limited by quantum fluctuations of the microwave field instead of thermal or technical noise. Applied to the detection of an ensemble of bismuth donors in silicon, the spectrometer reaches a sensitivity of 1700 spins detected within a single Hahn echo with unit signal-to-noise ratio [1]. This number is further increased in a second experiment by generating squeezed vacuum in the detection waveguide, reducing the amount of noise beyond the quantum limit [2].

Finally, the use of a high-quality-factor small-mode-volume ESR resonator also enhances the likelihood of spin relaxation by spontaneous emission of a microwave photon. This effect, predicted by Purcell, is large enough in our experiment to become the dominant spin relaxation mechanism. Sub-second relaxation times are achieved, a three-orders of magnitude enhancement compared to the non-radiative relaxation time. [3]. This provides a novel and general way to initialize spin systems on-demand.



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Hyperfine companions on a journey through the world of (bio)materials

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The use of hyperfine spectroscopic techniques dates back to the early days of ENDOR and its application has been further boosted by the introduction of multi-frequency pulsed EPR techniques. Although hyperfine spectroscopy can reveal properties undetectable by any other analytical tool, the complexity of the spectral interpretation very often limits its broader applicability. Using examples of my own research, I will be evaluating the potential, challenges and limitations of using modern-day hyperfine spectroscopy in (bio)materials research. This will also allow me to highlight many of the (hyper)fine companions that have guided me on my scientific journey.





Exploring Protein's Conformations *in Cells* with Gd(III) Spin Labeling

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Distance measurements between two spin labels attached at well-defined sites in proteins by double electron-electron resonance (DEER) spectroscopy have become an established structural tool in Structural Biology. Such measurements are carried out on frozen solutions and provide information on conformational distributions and conformational changes induced by ligand/substrate binding. The standard spin labels used for this purpose are based on nitroxide free radicals. In recent years we, and others, have demonstrated the utility of high frequency W-band, 95 GHz) DEER distance measurements in proteins using a new family of spin labels based on Gd(III) chelates.[1] These are particularly useful due to the high sensitivity at they exhibit at high magnetic fields and their chemical stability in the reducing environment of the cell cytoplasm. In-cell distance measurements require higher sensitivity than regular *in-vitro* measurements and therefore we have used broad band chirped pump pulses[2] in a slightly modified DEER sequence, which gave us a considerable increase in SNR. We will present examples of in-cell Gd(III)-Gd(III) distance measurements on several Gd(III) labeled proteins delivered into human HeLa cells using osmotic shock and electroporation.

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Two-dimensional distance correlation maps from pulsed triple electron resonance (TRIER) on proteins

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Recently we introduced the pulsed triple electron resonance (TRIER) experiment [1] as a complement to double electron-electron resonance (DEER): DEER usually provides distance distributions from doubly-labeled proteins. But if the investigated protein exists in more than one conformer, the peaks in the distance distribution cannot be unambiguously assigned. If a third spin label is added, the TRIER sequence allows for correlating dipolar frequencies that stem from the same molecule, which solves the assignment problem.

As compared to our first publication [1], we have improved the pulse settings and sequence as well as data processing and are now not only able to obtain better resolved spectra, but for the first time two-dimensional distance distributions. To this aim, we implemented a two-dimensional approximate Pake transformation as well as a gradient projection regularization algorithm for processing two-dimensional data sets. This allowed us to successfully apply the TRIER sequence to triply-labeled proteins and generate distance correlation maps (Fig. 1). We expect such maps to facilitate the interpretation of sets of DEER data and to give more insight into the structure of complex protein systems.

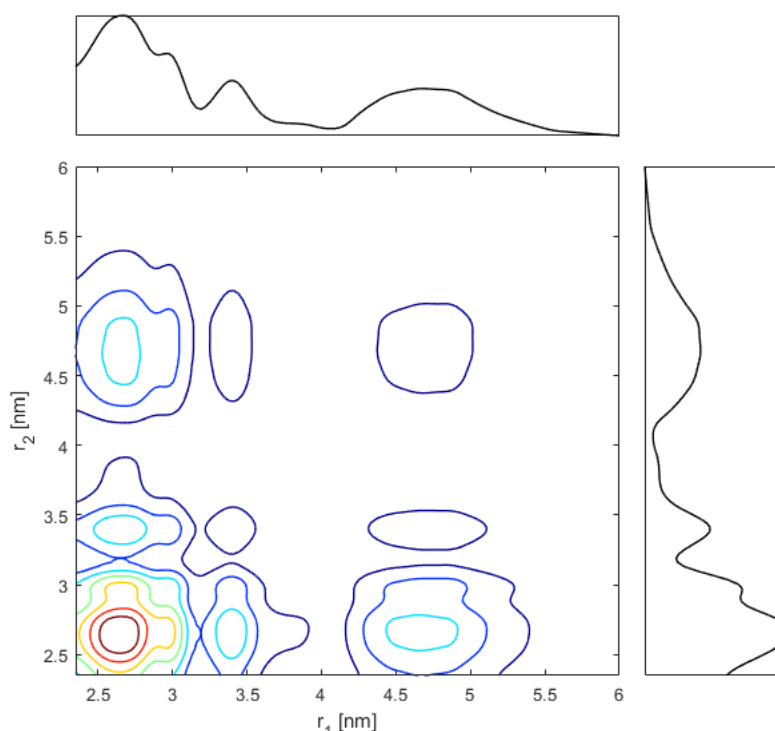


Fig. 1: Two-dimensional distance correlation map of the Rpo47 protein.

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Mechanically Interlocked Molecules: The Effect of the Mechanical Bond on the Magnetic Properties of Transition Metals Complexes

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In recent years, extensive research has been carried out on the construction of mechanically interlocked molecules for a wide range of functional applications. As well as their unique dynamic properties – exploited in the construction of molecular machines - rotaxanes possess peculiar features of mechanically interlocked ligand scaffolds able to bind a wide range of metal ions, whose properties can be profoundly affected by the mechanical bond [1]. We have recently shown that these ligands can enforce the formation of heteroleptic complexes with several first-row transition metals that do not form with acyclic counterparts and that possess unusual redox properties [2].

Co(II) was selected as a probe to investigate the effect of flexibility of the interlocked structure on the magnetic properties of the metal. We report the combined application of EPR spectroscopy and magnetic susceptibility measurements on three cobalt rotaxanes, where the central Co(II) ion is coordinated by three different macrocycles that together with the thread provide a pentacoordinate environment (Figure 1). The effective magnetic moment (μ_{eff}) values recorded at low temperatures, as well as X-band and Q-band EPR spectra acquired for

both powder and frozen-solution samples, revealed a sizable and negative D whose magnitude varies with the macrocycle even though the primary coordination sphere of the metal remains unchanged. The different saturation values of μ_{eff} and the contrasting EPR spectra also demonstrate that the high-spin to low-spin population ratio within each complex can be tuned by altering the macrocycle. The subtle modification of the interlocked ligands, as well as their unique ability to form a broad range of heteroleptic metal complexes, could thus enable the design of highly asymmetric transition metal complexes with tunable magnetic parameters, and potentially lead to new Single-Molecule Magnets [3].

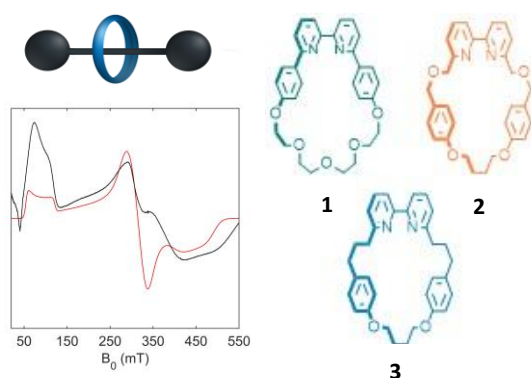


Figure 1. (Left) X-band CW spectrum of Co(2) and simulation (red). (Right) Macrocycle structures for the three Co(II) complexes investigated

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Magnetic edge states, spin dynamics and coherent manipulation of molecular graphene nanoribbons

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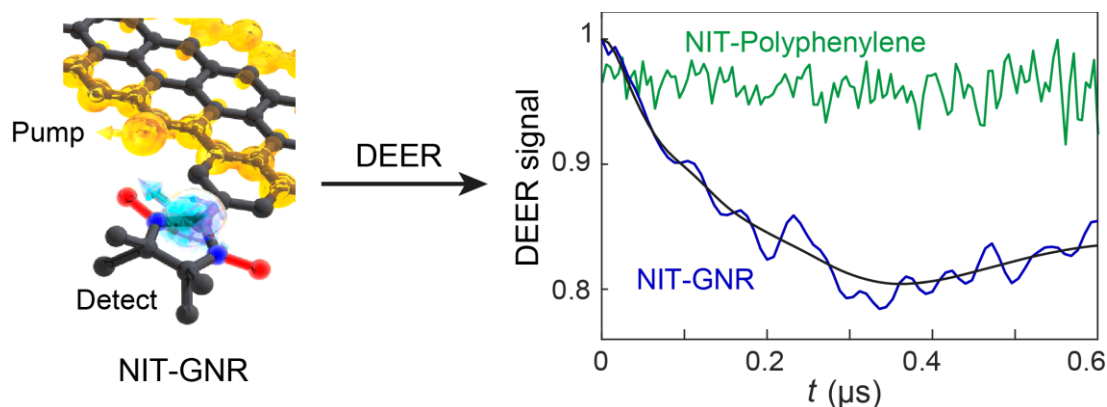
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Graphene, a well-defined two-dimensional network of carbon atoms, shows impressive electrical and mechanical properties [1]. By introducing magnetic edges in graphene nanoribbons, ferromagnetic couplings and superior spin filtering are predicted [2,3]. Conventional techniques such as unzipping of carbon nanotubes, however, do not deliver the necessary degree of purity to design such systems.

By utilising an ultra-clean synthetic approach, we were able to create graphene nanoribbons with great purity [4], and functionalize them with magnetic nitronyl-nitroxide radicals as magnetic sites. Using electron paramagnetic resonance spectroscopy, we gain a full picture of the interactions between the magnetic radicals. The coherence time reach microseconds at W-band frequencies at liquid nitrogen temperature, and sub-microseconds at room temperature. We obtained evidence of the existence of a magnetic edge state in the nanoribbon, a matter predicted 20 years ago and now clearly observed. Via double-electron-electron-resonance spectroscopy, we observed a coupling between the edge state and the radical spins, where we determined a two-qubit inversion time of 350 ns.



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Studying the structural changes of human Apoptosis Inducing Factor using spin labels

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Apoptosis Inducing Factor (AIF) is a NADH-binding flavoprotein located in the intermembrane space of mitochondria, anchored to the inner mitochondrial membrane. As the name indicates, this protein is involved in apoptosis, in a pathway independent of caspases. In response to specific death signals, AIF is proteolytically cleaved at residue 101 yielding the soluble apoptotic form that is released to the cytosol, and then translocated to the nucleus where it effects cell death.

In mitochondria, the protein exists in a redox-dependent equilibrium between dimeric and monomeric forms and is known to interact with a protein chaperone called CHCHD4. In addition, during its journey across the cell, AIF interacts with a number of other substrates and protein partners. The interaction with HSP70 induces cellular survival, while its interaction with nuclease cyclophilin A promotes the optimal nuclear translocation of both proteins. In the nucleus, AIF forms a ternary complex with histone H2AX and cyclophilin A that is able to bind and degrade DNA and promote programmed cell death.

NADH reduction of AIF produces dimerization of the protein which, according to the X-ray structures, is accompanied by conformational rearrangements of the reductase and apoptotic domains. In both, monomeric and dimeric forms, there is a flexible C-terminal segment of the sequence which is absent in the crystal structure. Whether this region can have different possible conformations or is totally/partially disordered is not known. Interestingly, there are observations which suggest some interconnection between the mitochondrial and apoptotic activities of AIF which increases the interest of the intriguing relation between redox state and structure.

In this contribution, we will show how the analysis of distance distributions between paramagnetic probes obtained by EPR can address the study of the relationship between conformational change, dimerization and redox state of the FAD cofactor. Moreover, the use of several distance constraints provides crucial help for modeling the disordered fragment.

The participation of this flexible loop in the interaction with its physiological substrates and partners throughout the different cell compartments can also be elucidated using EPR techniques.

Spin-signatures and dynamics of exchange coupled triplet excitons from singlet fission

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Spin plays a key role in the dynamics of organic semiconductors, with examples ranging from spin-dependent losses in organic photovoltaics and light-emitting diodes to magnetic field-dependent mobility in transistors. One such spin-dependent process, singlet fission, involves the production of two triplet excitons each with spin $S=1$ following excitation of one singlet exciton (spin $S=0$). This pair production process has the potential to boost the theoretical efficiency of photovoltaics beyond the Shockley-Queisser limit and has been used to produce photovoltaics with >100% external quantum efficiency [1,2]. Recently we have used singlet fission as a means of optically generating spin-

1 pairs to study the fundamental spin interactions of triplet excitons [3,4]. Using a combination of electron spin resonance and magneto-optical spectroscopy in high magnetic fields (<68 T), we observe and measure triplet spin-exchange coupling directly and extract values from 0.4-5.0 meV depending on pair conformation. These investigations have provided evidence for strong spin-coupling and high spin ($S=2$) formation in solid-state organic semiconducting materials. We further observe microsecond timescales for loss of coherence in the triplet pair state at low temperatures and model the time-dependent polarization of triplet states as a window into the spatial dynamics of triplet states. Spin interactions and coherence properties, such as those measured here in triplet exciton pairs, not only affect dynamic processes in electronic devices, but also present an opportunity for development of molecular spin-based technologies.

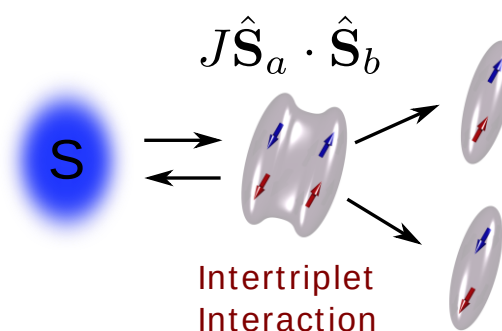


Figure: Triplet exciton pairs are formed from optically generated singlet excitons by singlet fission. ESR probes the spin-spin interactions of the triplets formed by singlet fission.

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When stronger magnets don't help: Methods for disentangling overlapping high-field EPR spectra illustrated in record organic solar cell blend PBDB-T:ITIC

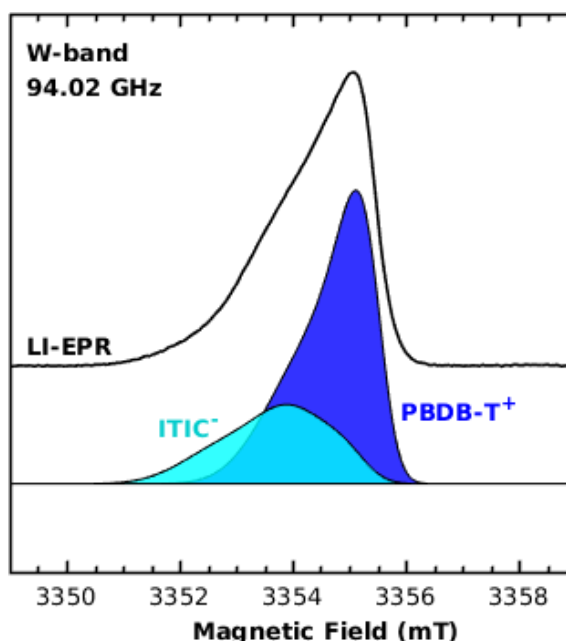
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Spectral overlap, even at high field, is a problem generally encountered in many EPR studies. In the specific case of bulk-heterojunction (BHJ) organic solar cells (OSCs), the paramagnetic species of interest are light-induced radicals which are created as a pair after charge transfer at the interface between the donor polymer and molecular acceptor regions making up the BHJ blend. Hence, the similar *g*-values expected for the positive and negative organic radicals often lead to strong spectral overlap complicating the unambiguous assignment of the light-induced (LI) EPR spectrum.

The donor-acceptor combination studied here, PBDB-T:ITIC, was the first fullerene-free OSC to recently achieve >11% efficiency, challenging the state-of-the-art polymer-PC₇₁BM devices [1]. For this blend, the two-component structure of the LI-EPR spectrum could not even be resolved at W-band frequency (94 GHz). Therefore we separated the two contributions to the total EPR spectrum by exploiting two different properties of the charge-transfer radicals, namely the (small) difference in their longitudinal (*T*₁) relaxation times and the presence of a unique magnetic nucleus, ¹⁴N, in the ITIC molecule. For the *T*₁-based method, we applied an inversion-recovery filter to selectively suppress one component in the spin echo analogously to the relaxation-filtered hyperfine spectroscopy (REFINE) technique first proposed by Maly et al. [2]. Sensitive detection of the ¹⁴N hyperfine couplings at W-band frequency was achieved by means of electron-electron double resonance (ELDOR)-detected NMR (EDNMR). Here we demonstrate the application of EDNMR-induced EPR to obtain a field-swept EPR spectrum containing only contributions from the ITIC radical [3]. Both approaches are validated by LI-EPR spectra on related blends which yield better resolved spectra of the individual PBDB-T and ITIC radicals.



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Metal centres in RIDME spectroscopy: methodology and application

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Relaxation induced dipolar modulation enhancement (RIDME) is attracting growing attention for long-range site-to-site distance measurements in biomolecules. In particular, the use of longitudinal relaxation events for spin inversion makes the technique very exciting for the application to spectrally broad metal centres. Intrinsically occurring metal ions in materials or metalloproteins and the possibility of substituting diamagnetic metal ions by paramagnetic ones provide a rich source of information for structure determination approaches. In addition, spin tags based on metal centres are a valuable supplement to the more commonly employed nitroxides allowing for spectroscopic selection schemes, which are based on at least two different types of spins. Moreover, some metal centres can be applied for the joint use of EPR together with paramagnetic NMR and are chemically more stable than nitroxides. High-spin S-state Kramers ions are particularly advantageous for pulse EPR measurements at high magnetic fields. However, the high-spin nature prevalent for some metal centres also gives rise to higher frequency overtones in the RIDME signal and complicates RIDME data analysis.¹

In this contribution, we want to discuss advantages and disadvantages of using low- or high-spin metal complexes for RIDME-based distance measurements. The case of low-spin complexes will be discussed by example of a Cu-Cu model compound before focusing on the methodological more challenging high spin Mn(II)^{2,3} and Gd(III)⁴⁻⁶ centres. We report on the consequences of higher frequency overtones for data analysis as well as their stability with respect to mixing time, measurement temperature, microwave frequency, field position of detection pulses and spin-spin distance, as well as first applications to biological systems: a polypyrimidine-tract binding protein and a DnaB helicase. Further, parameters influencing the choice of measurement conditions, the possibility of signal enhancement by prepolarization schemes, as well as factors determining the shape of the intermolecular background decay will be discussed.

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From EPR to DNP: Recent Developments in ENDOR and Liquid State DNP to Study Biomolecules

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Addressing the issue of sensitivity has been a long-standing goal in magnetic resonance, continuously leading to new hardware development as well as the design of new excitation and detection schemes. Our contribution in this direction has been the investigation of two different types of polarization transfer mechanism between electron and nuclear spins, specifically the electron-nuclear cross-polarization (eNCP or CP) in the solid state¹ and the Overhauser-type dynamic nuclear polarization in the liquid state. This lecture will give an overview on our recent insights and the application potential of these two methods in studies of biological systems.

We have introduced eNCP in ENDOR spectroscopy to elucidate the mechanism of proton-coupled electron transfer (PCET) in the catalytic reaction of the prototype enzyme ribonucleotide reductase. Using combinations of ²H-Mims and CP-edited ENDOR in conjunction with quantum chemical calculations we succeeded in determining the hydrogen bond network around catalytic intermediates as well as the conformation of the amino tyrosyl radical, a probe generally used in PCET reactions.² For studies in the liquid state, we recently observed that scalar electron-¹³C cross relaxation can lead to ¹³C NMR signal enhancements up to three orders of magnitude at various magnetic fields.³ These enhancements are consistent with theoretical predictions based on the available theory. Possible developments and applications of scalar Overhauser DNP will be discussed.

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Excited triplets of endohedral nitride cluster fullerenes: EPR / ENDOR study

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Multifrequency pulsed EPR/ENDOR spectroscopy was used to characterize the excited triplet states of a series of endohedral nitride cluster fullerenes with systematically varied metal cluster composition ($\text{Y}_3\text{N}@\text{C}_{80}$, $\text{Y}_2\text{ScN}@\text{C}_{80}$, $\text{YSc}_2\text{N}@\text{C}_{80}$, $\text{Sc}_3\text{N}@\text{C}_{80}$). The triplet lifetimes as well as the triplet quantum yields were found to strongly depend on the composition of the internal cluster. The prolonged stability of the triplet states at cryogenic temperatures allowed a detail characterization of the interaction between the two unpaired electron spins and the nuclei inside the fullerene cage.

Despite the dominant cage character of the spin density distribution, the W-band ENDOR investigations revealed a pronounced delocalization of the electron spin onto the internal cluster, which increased in the series from Y_3N [1] to Sc_3N . This has been rationalized based on the DFT calculations, which suggest a strong dependence of the spin density distribution on the cluster orientation inside the cage. The partial rotation of the smaller Sc_3N cluster in the excited state is thus predicted to be responsible for the larger cluster spin content in the $\text{Sc}_3\text{N}@\text{C}_{80}$ triplet.

From the methodological aspect, this study is one of the rare examples of high field EPR/ENDOR applications in the fullerene research. In addition to the improved resolution and sensitivity, the high field EPR experiments also require significantly smaller amounts of sample. This is a considerable advantage in the endohedral fullerene world, which notoriously suffers from low production yields. The benefits and drawbacks of the applied approach for future fullerene studies will be discussed.

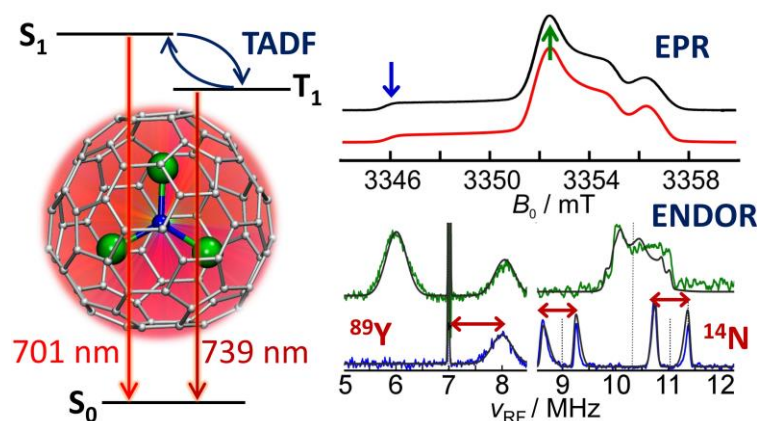


Figure 1. Efficient thermally-activated delayed fluorescence is found in endohedral fullerene $\text{Y}_3\text{N}@\text{C}_{80}$, and predominant localization of the exciton on the carbon cage is proved by ENDOR spectroscopy

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EPR investigations of potential molecular quantum bits

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Molecular quantum bits are paramagnetic molecules in which coherent superpositions of spin states can be generated. In contrast to initial predictions, low temperature coherence times are now approaching the millisecond regime and single quantum bit measurements were successfully carried out. Room temperature quantum coherence has been observed in a number of instances. The main advantage of molecular systems as compared to defect-based materials is the virtually limitless tunability, which enables placement of molecular quantum bits respective to each other with atomic precision.

Our own work in this area started with the demonstration of quantum coherence in high-spin ($S = 5$) single-molecule magnets about a decade ago [1]. We quantified the hyperfine couplings that limit coherence times by means of pulsed ENDOR [2]. From this we deduced the principle that removing weakly coupled nuclear spins from the immediate surroundings should be beneficial to coherence times, leading to a 68 μ s coherence time for $(\text{PPh}_4\text{-d}_{20})_2[\text{Cu}(\text{mnt})_2]$ (mnt^{2-} is maleonitriledithiolate) [3], which can be extended to hundreds of microseconds by means of dynamical decoupling methods. Interestingly, this system proved to be extraordinarily robust to changes in frequency. Recently our work has been geared towards studying thin films of these materials with the ultimate aim of generating and investigating ordered two-dimensional arrays. To this end we have studied transition metal phthalocyanines which proved to possess favourable spin dynamics properties [4]. Another class of materials are transition metal diketonates, which can be sublimed. Interestingly, we were able to predict the coherence decay of doped powder samples on the basis of the crystal structure alone [5]. We will also present our unpublished work in developing resonators to study thin films and first studies of such films.

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Low-Valent Nickel(I) Complexes Stabilised by RE-NHCs: Synthesis, EPR/DFT Studies and Catalytic Activity

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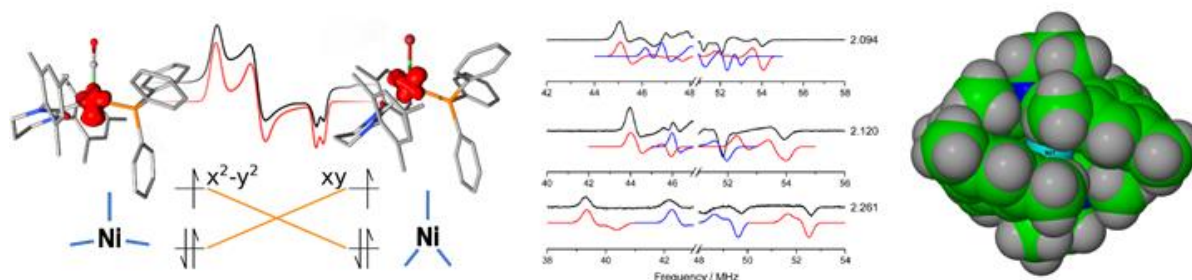
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Ni(I) complexes have recently been identified as a rare oxidation state of growing importance, due to their involvement in enzymatic activity and as replacements for expensive precious metals in a wide variety of organic transformations. We have recently reported the isolation of a wide range of three- and two-coordinate Ni(I) species stabilised by so-called ring expanded NHCs (RE-NHCs; carbenes with ring sizes >5) [1,2], and characterised the electronic structures through CW X-/Q-band EPR and Q-band 1H ENDOR measurements.

Treatment of [Ni(6-Mes)(PPh₃)Br] with a variety of bromide abstracting reagents has yielded a series of new mono- and dinuclear nickel products. Of most interest are the three-coordinate d⁹ complexes of general formula [Ni(6-Mes)(PPh₃)X]^{0/+} that distort from ideal D_{3h} symmetry by forming either T- or Y-shaped geometries. The overall computed spin densities in this series are polarised differently for the Y- and T-shaped complexes, which directly affects the shape and magnitude of the g-tensor [3].

We are currently exploring the activity of these complexes in C-C cross coupling and hydrodehalogenation. Furthermore, DFT calculations reveal significant magnetic anisotropy arising from orbital degeneracy in the two-coordinate cationic [Ni(6-Mes)₂]Br, leading to single-ion magnet (SIM) behaviour.[4]



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Studying Conformations of Oligonucleotides with Pulsed Dipolar Spectroscopy

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Oligonucleotides perform a broad range of functions within cells. For example: DNA stores the genetic information and the telomeres are also involved in aging. RNA is the mediator, which transforms the genetic information from DNA into proteins and is involved in gene regulation and RNA maturation. All these functions go along with a wealth of different structures, complex formation and conformational changes during function. Thus, biophysical methods are needed which can reveal the structures and conformational dynamics on the relevant size and time scale. In this regard, EPR spectroscopy offers the possibility to study large oligonucleotide structures and complexes on the nanometer scale and with time resolution.

In the presentation, the spin labeling of long RNAs based on click chemistry [1] and splinted ligation will be shown for a tetramethyl- and a tetraethyl-nitroxide. The tetraethyl nitroxide has the advantage that T_m relaxation times of around 20 μ s are achievable in frozen solutions. Applications of these labeling strategies in combination with cw EPR and PELDOR/DEER are then used to follow the metal ion and ligand induced folding of the preQ1 riboswitch. Using Cu(II) as spin labels it will also be shown that the structural building blocks of telomeres, the G-quadruplexes, can adopt different folds in dependence of the monovalent ions. Finally, the presentation will report on two methods for obtaining time resolution for conformational changes monitored with EPR. One employs a mixing resonator, which works at room temperature and on the millisecond time scale [2]. The other is Hyper-Freeze-Quench and works in the frozen state on the microsecond time scales.

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Exploring reliable distance measurements and dipolar correlations in an orthogonally labelled three-spin system

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As the amount of dipolar information encoded increases with the number of spin labels present within a system, the use of multi-spin systems for electron paramagnetic resonance (EPR) based pulsed dipolar spectroscopy (PDS) is an attractive option for optimizing the amount of inter-spin distance information that is gained from a single sample. However, if all the spins-labels are of the same type, it is not possible to determine which part of the measured distance distribution corresponds to the interaction between a specific pair of spins. The application of orthogonal labelling, using different types of spin labels, to multi-spin systems provides the potential to measure individual pairwise interactions [1].

In this work, we use an orthogonally labelled three-spin model system containing trityl, nitroxide, and Cu(II) porphyrin spin centres, with unique distances between each pair, to demonstrate how relaxation filtration techniques (REFINE) [2] in combination with Double Electron-Electron Resonance (iDEER from DEER or PELDOR), [3] and Relaxation Induced Dipolar Modulation Enhancement (RIDME) [4] can be used to extract the three different inter-spin distance distributions.

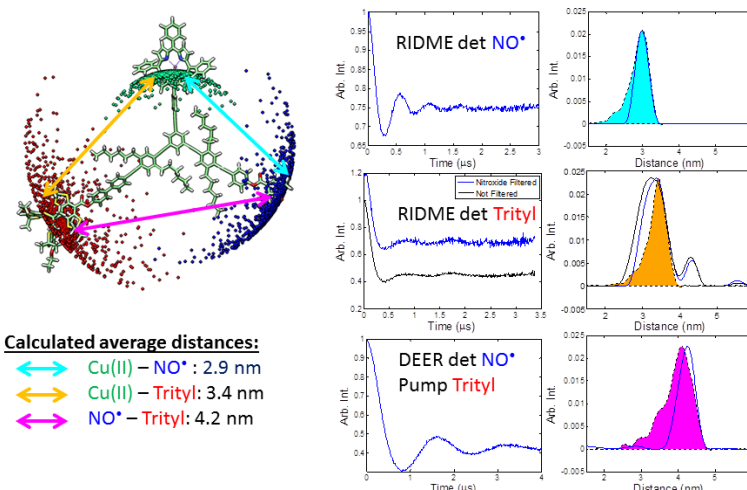


Fig: A) Structure of the model system with calculated distributions and average inter-spin distances. B) Dipolar traces recorded under conditions to probe different pairwise dipolar interactions.

Although measuring the pairwise interactions individually allows analysis of specific inter-spin distances, these methods cannot distinguish between orthogonally labelled systems in which all the spins are interacting simultaneously and those where they are not. Such information could be very important if the interacting spin labels are not all bound to the same molecule, but rather bound to different molecules which may or may not interact. We explore how combinations and extensions of DEER and RIDME-type experiments can be used to demonstrate multi-spin interactions.

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In-cell PELDOR spectroscopy on spin-labelled RNAs

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In-cell structural studies on biomacromolecules are motivated by the presence of factors characterizing the intracellular environment which are difficult to mimic *in vitro*. These include its highly crowded nature as well as the presence of a multitude of molecules which can act as binders towards the investigated system, possibly affecting its conformation.

For the purpose of this study two spin-labelled double-stranded RNA oligonucleotides, differing by the strategy with which the spin-bearing moiety has been introduced, have been internalized by microinjection into *Xenopus laevis* oocytes.

In the first case, a self-complementary 24-mer dsRNA has been spin-labelled by a post-synthetic method whereby a 2'-amino uridine, introduced into the RNA sequence with the use of the corresponding commercial phosphoramidite, is conjugated with an aromatic isothiocyanate derived from an isoindoline nitroxide [1]. For this kind of construct three sets of spin-labelled oligonucleotides have been prepared differing only by the position of the 2'-amino uridine within the sequence. In the second case, a spin-labelled 20-mer dsRNA has been obtained by incorporation of a spin-labelled uridine analogue bearing an isoindoline-derived benzimidazole nitroxide spin label [2]. The two strategies differ by the mobility of the spin label with respect to the RNA backbone; more in detail, the spin-labelled uridine analogue is characterized by a restricted rotation around the single bond linking the spin label to the uracil, resulting in a conformationally unambiguous tag. In both cases protection of the spin-bearing moiety against reduction in the intracellular environment was achieved by replacing the four methyl groups flanking the N–O moiety in conventional nitroxide spin labels with ethyl ones [3].

The conformation of the RNA constructs has been probed both in solution and inside cells by using PELDOR spectroscopy to report on the distance between two spin labels introduced on the two complementary strands of the double-stranded constructs. The major challenge associated with in-cell PELDOR measurements with respect to measurements on samples prepared in solution is related to the weaker observed spin echo signal, which is caused on the one hand by poorer sample packing efficiency and on the other hand by faster transversal spin relaxation. For samples characterized by inter-spin distances longer than 3 nm overcoming these limitations required the use of new techniques, namely the 5-pulse PELDOR sequence [4] with adiabatic inversion pulses [5], which allow extending the accessible dipolar evolution time window with respect to the conventional 4-pulse PELDOR experiment.

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Mechanical activation of an ion channel by chemical modification of pressure sensitive nano-pockets

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Mechanical activation of ion channels is caused by changes in membrane tension and must occur through protein sites accessible to the lipid bilayer [1]. Mechanosensitive (MS) channels sense and respond to force, by altering their structure and function [2]. Amongst all known ion channels, the MS channel of large conductance (MscL) has the highest-pressure activation threshold and requires over 12mN/m to achieve mechanical stimulation.

We have tested multiple protein sites and identified well defined pressure-sensitive nano-pockets within MscL's transmembrane region, not directly exposed, but accessible to lipid chains. We coupled PELDOR (DEER) spectroscopy with SDSL [3,4] and promoted channel opening via cysteine modification, in the absence of pressure.

PELDOR distance measurements of MscL in solution and lipids accurately assigned channel's conformational transitions. NMR and lipid ES-MS lipid analyses suggested that MscL has preference but not specificity, to endogenous membrane lipids. Atomistic molecular dynamic simulations of the spin labeled channel embedded within lipid bilayers, showed that only specific spin label conformers restrict lipid chain access to the nano-pockets. Comparison of single molecule recordings in lipid bilayers between the modified and native protein suggested that the modification does not alter MscL function.

We showcase spin label's dual role as an EPR reporter and potential trigger for MS channel activation. Manipulation of MS channel pores through targeted modification of nano-pockets could constitute a potential new tool for ion channel regulation.

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Temporal mapping of excitonic wavefunctions with carbon specificity

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Organic semiconductors fall into a class of materials that shows significant potential for future applications, due to their ease of processing, low cost, highly tuneable electronic properties, favourable mechanical properties and long spin coherence times. However, there is a lack of suitable techniques that can yield information on intrinsic spin dynamics in organic materials, particularly when they are in the excited state. Muon spin spectroscopy is a technique that has rarely been applied to study excitonic problems in organic systems, yet it's local nature is ideally suited to studying them [1-4]. I will discuss some recent results on exciton dynamics in TIPS-Pentacene [5], using the newly commissioned photo-muSR setup on the ISIS HiFi spectrometer. I will show that muons are sensitive to the time evolution of triplet excitons with a spatial resolution of individual and specific carbons on the backbone of the molecule, and discuss their role in the photochemical reactions of TIPS-Pentacene.

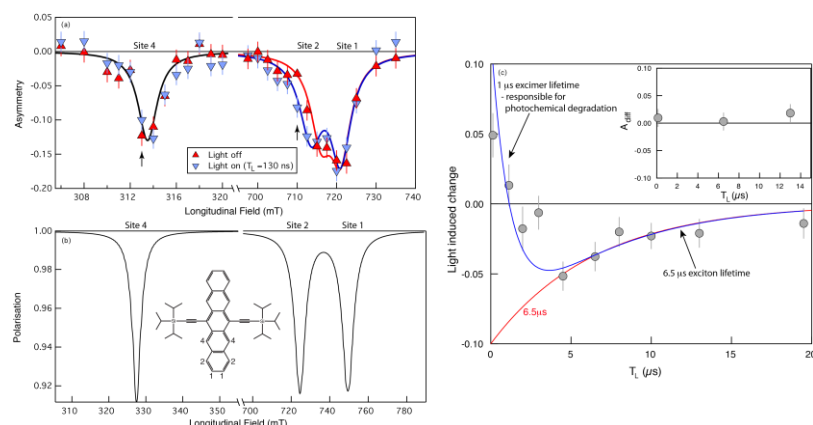


Figure 1: (a) ALC spectra for three different muonium bonding sites on the backbone of the molecule (see the inset to (b) for a diagram). Light induced changes are observed in the line shapes for only two of the three sites, corresponding to the end of the molecule. (b) DFT calculations that predict the ALC resonance fields, which can be used to assign bonding sites (see inset). (c) The time dependence the light-induced signal for site 2, where two timescales can be seen. A 1 μ s signal corresponding to a dimer state (likely a singlet fission product, and a precursor to the final triplet excitation), and a 6.5 μ s signal corresponding to the triplet exciton lifetime. No light induced signal is observed for the neighbouring site 3, as can be seen in the inset.

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Uniform Field Resonators for Correlation Spectroscopy Methods at Q-band

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Correlation spectroscopies, such as ESEEM/HYSCORE, provide information on the interactions of a paramagnetic center with its surrounding nuclei, while PELDOR provides information on interactions between paramagnetic centers. These pulse EPR spectroscopies rely on information provided by the spin-spin coherences induced by the incident resonant microwave field. However, in typical microwave cavities the incident microwave magnetic field has cosine dependence along the length of the sample. Therefore, the non-uniform magnetic field will excite an array of over and under tipped spins along the axis of the sample. A non-uniform microwave field incident on the sample affects the time domain EPR signal profile, EPR signal amplitude, and can even lead to complicated non-linear backgrounds.

A Re-Entrant TE_{01U} at Q-band (34 GHz) was designed, fabricated, and tested [1]. The novel re-entrant geometry lowers the cut-off frequency of the waveguide by concentrating the electric field between the re-entrant fins, illustrated in Fig. 1A. This increases the stored energy of the resonator and increases the overall resonator conversion factor ($\text{mT}/W^{1/2}$) while providing an 85% uniform incident magnetic field over a 10 mm region-of-interest, illustrated in Fig. 1B. In order to match the cut-off region, two Rexolite end sections are fabricated.

The Re-Entrant TE_{01U} resonator, with a Q-value of 1800 and an over-coupling coefficient (β) of 3.5, is well suited as a resonator for pulse EPR experiments. Due to the increase in stored energy and the uniform magnetic field, no signal loss is exhibited compared to a cylindrical TE₀₁₁ resonator under similar conditions. In this presentation, experimental data are shown using a number of pulsed methods compared to a TE₀₁₁ cavity. For example, Fig. 2 shows the results of a nutation experiment on BDPA in polystyrene. Significant improvement is shown comparing a TE₀₁₁ cavity (Fig. 2A) to the uniform Re-Entrant TE_{01U} cavity (Fig. 2B). Further improvement is shown when the sample is confined to the region-of-interest (Fig. 2C). Finally, extension to W-band (94 GHz) is discussed.

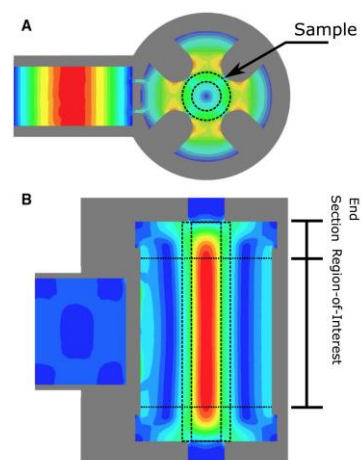


Fig. 1: Ansys HFSS simulation of the Q-band Re-Entrant TE_{01U} geometry showing A) electric and B) magnetic microwave field.

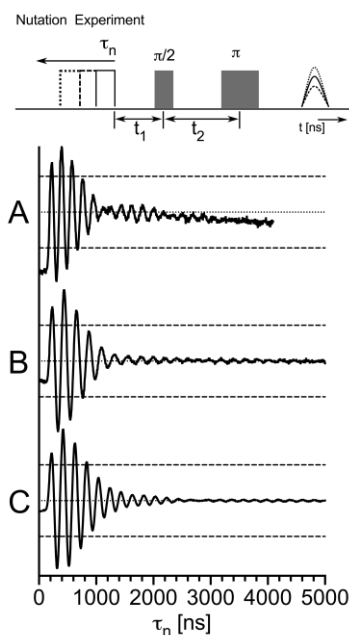


Fig. 2 Nutation experiment on a BDPA sample performed using the A) cylindrical TE₀₁₁ cavity B) and the uniform Re-Entrant TE_{01U} cavity with the sample extending the entire length and C) a 9.5 mm sample centered in the region-of-interest.

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Meeting the Sensitivity Grand Challenges in Pulsed EPR

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Possibly the single biggest grand challenge for the majority of EPR applications is to improve the concentration sensitivity for pulsed and direct detection measurements, particularly in broad-line, fast relaxing, paramagnetic systems. In this talk, I will outline the vision of a new research program that is seeking to improve concentration sensitivity by more than an order of magnitude over existing high power W-band systems [1] that already exceed the sensitivity of the best commercial high power Q-band systems. If this can be achieved then it starts to become possible to characterize long-range structure and dynamics of proteins and protein assemblies close to physiological concentrations (< 100 nM). A secondary aim is to dramatically improve time resolution, and to be able to make sensitive zero dead-time measurements *during* kW pulses, on spin labeled nitroxide systems at concentrations as low as 100 μ M, potentially allowing the motional dynamics of very fast relaxing centres to be characterised. A third aim is to investigate various pulsed solid-state DNP strategies and to significantly increase the sample volume associated with current liquid state (aqueous) DNP techniques.

Preliminary results and a broad overview of the challenges and opportunities will be presented.

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Cryogen Free Superconducting Magnets for Solid State NMR and DNP Applications

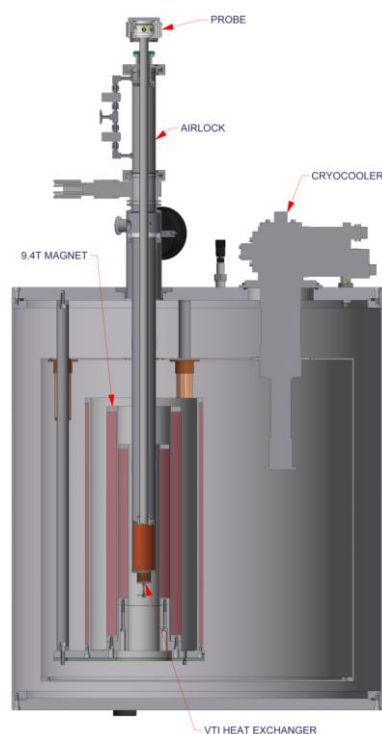
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²Talavera Science, Harrogate, UK.

We present 9.4 T and 12.1 T superconducting magnet systems for low temperature solid state NMR and DNP applications. The systems are equipped with integrated variable temperature inserts (VTI) cooled by a single GM or PT type cryocooler to both magnet and VTI. Sample insertion into the cold sample space is via an airlock mechanism. Temperature of sample controlled within 0.1K by close cycle helium gas flow through VTI tube. Nominal sample base temperature of the VTI in continuous operation is 1.6 K, although 1.3 K is comfortably achieved with a larger dry circulation pump. To improve field homogeneity we utilise a set of four or eight superconductive shim coils. The cryostat incorporates permanently mounted HTS current leads, which allow the magnetic field to be varied from zero to maximum field with high resolution. Cryocooler endurance is typically greater than 20,000 hours between service intervals.

When the magnet is not in use it can be conveniently switched off and restarted at a later stage without requiring extensive experience. In the case of a magnet quench event the magnet will cool down ready for operation within a couple of hours, without any user intervention.



Cryostat specification

- Diameter – 800 mm
- Height to airlock – 1100 mm
- Sample access diameter – 30-50 mm
- Total weight – about 200 kg
- Cold head type -1.5W GM or 1W Pulse Tube
- Cool down time from room Temperature – 48 hours

Magnet specification

- Sweep range 0-9.4 T
- Bare magnet homogeneity – 20 ppm within 10 mm dsf
- Number of sc shim coils – non, 4 or 8
- Homogeneity with 4 sc shims – 2 ppm, with 8 sc shims – 0.5 ppm within 10 mm dsf
- Field drift less than 0.1 ppm/hour

A Bifunctional Spin Label for Ligand Recognition on Surfaces

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In situ monitoring of biomolecular recognition, especially at surfaces, still presents a significant technical challenge. Electron paramagnetic resonance (EPR) of biomolecules spin-labelled with nitroxides can offer uniquely sensitive and selective insights into these processes, but new spin-labelling strategies are needed. We report the synthesis and study of a bromoacrylaldehyde spin-label (BASL), which features two attachment points with orthogonal reactivity (Figure 1). We have created the first examples of mannose and biotin ligands coupled to aqueous carboxy-functionalized gold nanoparticles through a spin-label. EPR spectra were obtained for the spin-labelled ligands both free in solution and attached to nanoparticles. The labels were recognised by the mannose-binding lectin, Con A, and the biotin-binding protein avidin-peroxidase. Binding gave quantifiable changes in the EPR spectra from which binding profiles could be obtained that reflect the strength of binding in each case. [1]

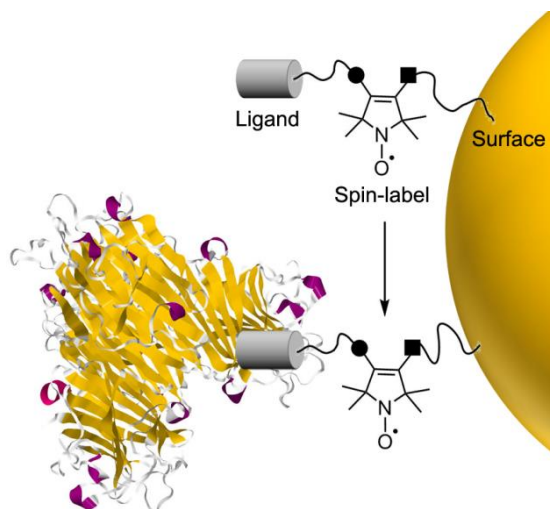


Figure 1. The concept of using a bifunctional spin-label for studying surface-ligand binding to proteins.

[1] M.A. Hollas, S.J. Webb, S.L. Flitsch, A.J. Fielding, *Angew. Chem. Int. Ed* **2017**, 56, 9449-9453

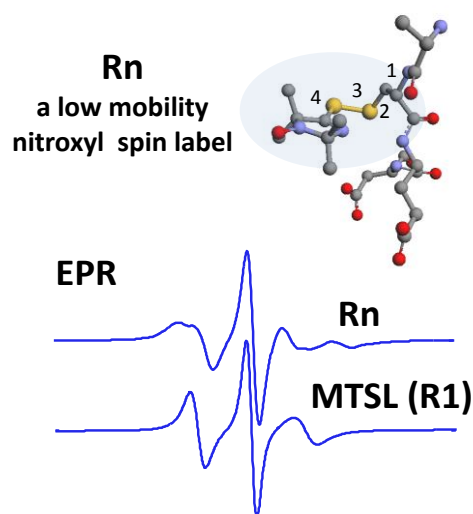
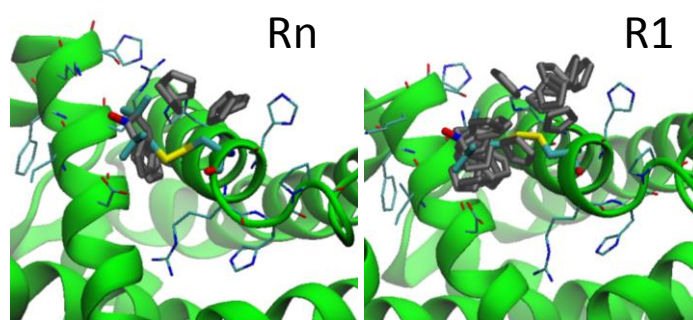
Rn - a spin label with limited internal mobility sensitive to protein dynamics: evidence from a combined EPR and Molecular Dynamics simulation study

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The bi-radical bis-(2,2,5,5-Tetramethyl-3-imidazoline-1-oxyl-4-yl) disulfide (RnSSRn) was developed primarily for the quantitative determination of SH groups in proteins using EPR [1]. Like MTSL, it reacts readily with the thiol side-chain of cysteine to give a nitroxyl spin label, Rn, however, its potential as a probe of motion has been little explored.

Our recent EPR studies combined with fully atomistic Molecular Dynamics (MD) simulations and the MD-EPR prediction method [2,3], developed and successfully applied by us to various soft matter and protein systems previously [2-6], provide evidence for intrinsic low rotameric mobility of Rn, compared to widely employed label MTSL (R1). Both experimental and modelling results using structurally different sites of attachment to Myoglobin show that the EPR spectra of Rn are more sensitive to the local protein environment than that of R1 [7]. The flexibility of Rn is comparable to the one of R1 placing it in favourable position relative to highly rigid spin labels that might perturb the structure. Our results demonstrate that in cases where the dynamics of R1 is approaching fast motional regime with motional contributions averaged out Rn offers a better choice to discern protein dynamics. This suggests the use of Rn in CW EPR experiments as a complementary probe to the widely applied MTSL (R1) in order to provide a sensitive reporter on the protein motions [7]. Implications for the use of Rn label in DEER/PELDOR measurements are discussed.



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The Spin as Probe for Structure and Function in Metal Biocatalysis

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In biology many catalytic reactions are performed by metalloenzymes. These are often paramagnetic at least in some of their intermediate states and can advantageously be studied by modern EPR techniques. Metal centers are involved in such interesting processes as catalytic water oxidation, nitrogen fixation and hydrogen production/consumption. In this lecture the enzymes water oxidase and hydrogenase are discussed as examples.

Light-induced water splitting and oxygen release is performed by a protein-bound $\text{Mn}_4\text{O}_5\text{Ca}$ cluster located in photosystem II (PSII) of photosynthetic organisms; the structure has been obtained by X-ray crystallography [1]. Details of the cluster's electronic structure in the various states of the enzymatic cycle are available from cw/pulse EPR and double resonance technique like ^{55}Mn ENDOR [2]. ELDOR-detected NMR (EDNMR) enabled the detection of the binding of the first substrate water (using H_2^{17}O exchange) to the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster [3]. The state directly preceding the O-O bond formation could also be analyzed by EPR techniques leading to a model for the binding of the second water molecule [4]. Based on these data and together with quantum chemical approaches a robust model for the mechanism of water oxidation in PS II has been developed [5].

The [NiFe] and [FeFe] hydrogenases contain bridged binuclear transition metal cores in their active sites, which are tuned by a special ligand environment (including CO and CN^- ligands) to convert protons to molecular hydrogen or *vice versa* with very high efficiency via a heterolytic splitting mechanism. The various intermediate states in the catalytic cycle have been investigated by an array of spectroscopic techniques, where EPR played a prominent role [6]. Enzyme activation and inhibition (e.g. by CO or O_2), as well as substrate binding and product formation were studied and led to proposals for the catalytic cycles of these hydrogenases [7, 8].

The information gained from studying the natural enzymes is very valuable for the design of bioinspired catalysts, e.g. for hydrogen conversion and production [8].

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Taming defects in diamond

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Defects in diamond have great potential for use as quantum sensors and qubits. The negatively-charged nitrogen-vacancy (NV⁻) centre in diamond is established as a leading platform in solid state quantum applications, with potential technologies in sensing, computation and communication enabled by its long spin-coherence time and optical spin polarization. However, NV's poor photonic properties (Debye-Waller factor ~ 0.04) have resulted in significant efforts on optical cavities to enhance its coherent emission, and search for alternate colour centres with comparable spin properties and superior optical properties.

Currently, the vacancy-impurity family of defects is most promising, with major interest in group IV centres SiV⁻ [1,2], GeV⁻ [3] and SnV⁻ [4,5]. Of these, SiV⁻ is the most-studied, with $T_2 > 10$ ms and single-shot readout demonstrated at 100 mK. Nonetheless, the onerous experimental requirements and low quantum efficiency ($\sim 10\%$ [6]) motivate further research on alternative centres. In this presentation, I will discuss recent work alternative colour centres, including the neutrally-charged silicon vacancy, SiV⁰ [7,8], its spin physics and electronic structure.

Full exploitation of their optical and spin properties necessitates that we control the position, orientation and environment of the chosen colour centre to optimise all of the desirable properties simultaneously, especially near the surface of the diamond. I will review our understanding of the production of intrinsic defect complexes and present new data on the production defect complexes by doping, electron irradiation, short pulse laser irradiation, ion implantation and annealing.

This work is supported by EPSRC grants EP/M013243/1, EP/L015315/1, EP/J500045/1, the De Beers Group of Companies, the Gemological Institute of America, the UK Quantum Technology Hub: NQIT - Networked Quantum Information Technologies and the EPSRC Centre for Doctoral Training in Diamond Science and Technology

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Continuous-wave room-temperature maser using NV centres in diamond

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The solid-state maser, invented in the 1950s, has had a less illustrious career than its younger sibling, the laser. This is mainly due to its dependence on cryogenic refrigeration and high-vacuum systems. Despite this, the maser has found application in deep-space communications and radio astronomy due to its unparalleled performance as a low-noise amplifier and oscillator. In 2012, the first room-temperature solid-state maser was demonstrated, exploiting the photo-excited triplet state of pentacene molecules in a *p*-terphenyl host [1], paving the way for a new class of maser. Since then, the maser has been miniaturized [2], characterized on nanosecond timescale [3] and shown to demonstrate strongly coupled ensemble spin-photon polaritons [4]. However, *p*-terphenyl has poor thermal and mechanical properties, and the triplet sublevel decay rates of pentacene mean that only pulsed operation has been observed in this system to date. Alternative materials may therefore be required to achieve continuous emission and inorganic materials containing spin-defects such as diamond [5] and silicon carbide [6] have been proposed. Here we briefly report a continuous-wave (CW) room-temperature maser oscillator using optically pumped charged nitrogen-vacancy (NV⁻) defect centres in diamond [7]. This demonstration unlocks the potential of room-temperature solid-state masers for use in a new generation of microwave devices that could find new applications in spectroscopy, medicine, security, sensing and quantum technologies.

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NO₂ adsorption in porous metal organic frameworks (MOFs) investigated by electron paramagnetic resonance

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Nitrogen dioxide (NO₂) is a major air pollutant, known to cause significant environmental problems [1]. As such, its removal from atmosphere is a pressing matter. One promising approach is the use of robust metal organic frameworks as NO₂ adsorbents. However, no MOF system was demonstrated so far to reversibly adsorb NO₂, despite clear evidence of NO₂ retention in metal organic frameworks [2].

This lecture will discuss the first pulsed EPR studies focusing on the reversible adsorption of NO₂ in an ultra robust metal-organic framework, MFM-300(Al/Zn) [3]. The NO₂...MOFs interactions were studied by a combination of continuous-wave and pulsed-EPR methods, which provided valuable insights into the adsorption mechanisms. The NO₂ uptake is fully reversible, and the host material can be regenerated with full retention of its structure and sorption capacity for at least five cycles. The supramolecular binding of other gases, such as CO₂, was also examined, in the redox active paramagnetic MOF system, MFM-300(V) [4].

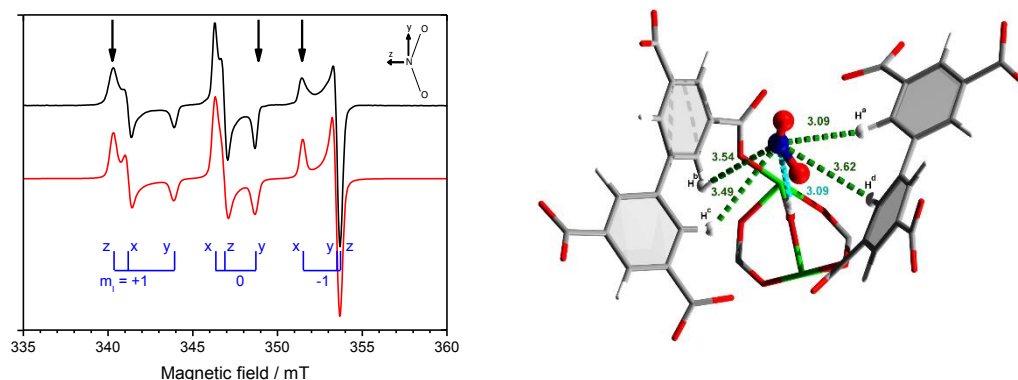


Fig. 1 CW X-band EPR spectrum at 40 K (black) and simulation (red) with $g_x = 2.0052$, $g_y = 1.9915$, $g_z = 2.0021$ and ¹⁴N nuclear hyperfine constants of $A_x = 144$, $A_y = 135$, $A_z = 185$ MHz, where x, y and z define the NO₂ molecular axes (inset).

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Double resonance calibration of g factor standards: Carbon fibers as a high precision standard

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The precise determination of the g factor is important in many applications of EPR spectroscopy. Unfortunately, the magnetic field B_0 at the sample position is not usually known with sufficient precision for determining the absolute g factor. Therefore, one usually measures a sample with known g factor (“the standard”), either shortly before (calibration) or together (internal standard) with the sample of interest. Established standards like DPPH, Mn:MgO or Li:LiF show difficulties in handling, reproducibility or precision. Newer proposals like H@iBuT₈ are not easily available. Furthermore, many existing standards which are easy to handle as internal standards, are not independently calibrated and therefore lack precision.

We propose high performance carbon fibers as a new general-purpose g factor standard [1]. Carbon fibers show exceptional ESR properties like a perfectly Lorentzian rather narrow line (0.4 G @ 4.2 K), a $g=2.002644(30)$ factor near g_{free} and a rather strong signal. Moreover, carbon fibers meet the requirements in practice because they are easy to handle, inert and very cheap. However, what counts most is that carbon fibers are absolutely and independently calibratable by internal protons. For calibration, we measured the proton nuclear resonance and the ESR transition frequency simultaneously with high precision, as only frequency ratios are important. The nuclear resonance is detected via the Overhauser shift which is considerably enlarged due to DNP [2]. Our double resonance experiments enabled us to determine the g factor up to a relative uncertainty of ± 15 ppm. This lets carbon fibers compete with established high precision standards like Li:LiF [3].

We believe that research along our lines will open the door to a whole class of new possible g factor standards where the precision can be pushed even further. The calibrated high-performance carbon fibers are fully operational and satisfy today's demands on precision for many experiments. The easy handling, the “intertness” and the strong signal make carbon fibers an ideal standard for the day-to-day usage in many laboratories worldwide even in cases where such high absolute precision is not needed.

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Iron One

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Highly reduced low-coordinate base metal complexes featuring β -diketiminato ligands have shown to be able to activate a plethora of challenging chemical bonds. However, the negative potential required for metal-centered reduction requires the use of harsh reductants that are often incompatible with exogenous substrates for catalytic transformations. Formazanate is a variant on the archetypal β -diketiminato ligand, and with the unoccupied ligand orbital low in energy, it makes complexes with this ligand easier to reduce. Formazanates undergo more facile ligand-centered reduction when bound to boron and zinc, but this feature has not yet been with a redox-active transition metal ion. Herein, the reactivity of formazanate complexes of iron is detailed, and reveals ligand-centered reduction at relatively mild potential. The electronic structure of the formally iron(I) species is more accurately described as iron(II) with a coordinated formazanate radical dianion [1]. This complex is contrasted with the recent and surprising report of an iron(I) centre stabilised within a fully oxidised polyoxovanadate ligand [2]. Careful scrutiny of the evidence reveals this claim to be complete hogwash.

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Multi frequency EPR study of novel paramagnetic diazadiene complexes of alkali metals lithium and sodium

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1,4-diaza-1,3-dienen (DAD) ligands have received a lot of interest in coordination and organo-metallic chemistry. They could go easily under redox reactions and have shown the possibility of chemical modifications on both carbon and nitrogen sites in a wide range. Although there are several studies on radicals of heavy main elements and transition metals of DAD ligands, there are fewer studies on the group I metal complexes of these ligands [1].

Herein, we report the electronic and molecular structures of novel paramagnetic alkali metal (lithium and sodium) complexes of DAD, fully characterized using a multi-frequency electron paramagnetic resonance (EPR) spectroscopy approach. EPR measurements, using T_1 relaxation-time filtered pulse EPR spectroscopy [2,3] revealed the diagonal elements of **A**- and **g**-tensors for metal and ligand sites. It is found that the central metals in the lithium complexes have a sizable contribution to the SOMO while this contribution is less strongly observed for the sodium complex [4].

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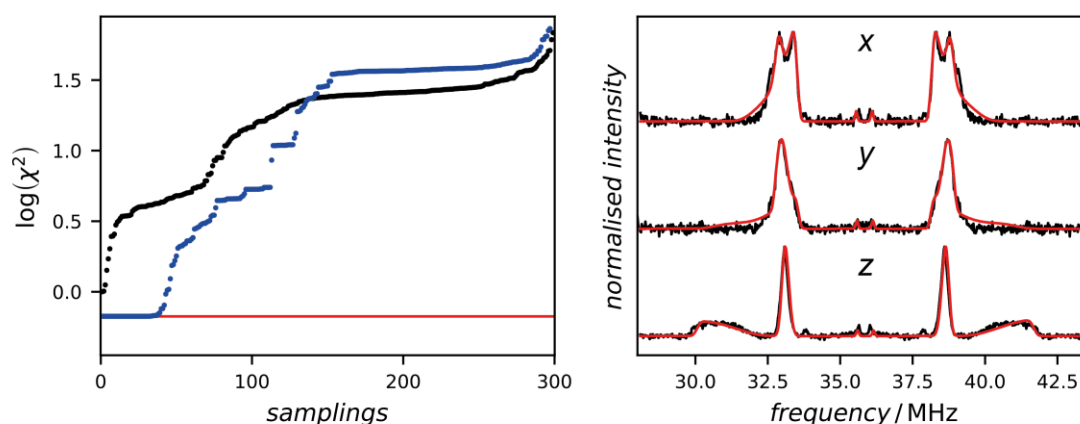
SpecProFi: A new comprehensive EPR data processing and fitting framework

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Analysing EPR data is quite often a complicated and crucial challenge, particularly in case of many unknown spin-system parameters which have to be determined in an optimisation procedure fitting spectral simulations to experimental results.

Here, we present SpecProFi (Spectra Processing and Fitting), a new comprehensive EPR data processing and fitting framework written in MATLAB and providing sophisticated tools like global analysis of multiple experimental data sets combined with a semi-stochastic approach (Figure, left). Such global analyses include the simultaneous analysis of cw-EPR measurements at multiple microwave frequencies, cw-EPR and ENDOR spectra, orientation-selective ENDOR data recorded at different magnetic field positions (Figure, right), multiple harmonics or liquid- and solid-state cw-EPR data. SpecProFi relies on the well-established EasySpin simulation package [1] and retains the corresponding parameter syntax, making it easy to use. Beside the fitting framework, SpecProFi provides various independent functions for data processing, such as denoising methods (based on either discrete wavelet transform or conjugated Fourier space methods), automatic phase-correction for cw-EPR data, and differentiation of absorptive EPR data using Tikhonov regularisation.



While EasySpin is a very elaborated and powerful collection of simulation routines, due to its closed-source nature it cannot be extended on own initiative. Spin-correlated radical pairs, e.g., are currently not treated in EasySpin. Therefore, we developed a highly efficient and robust simulation kernel for solid-state cw-EPR spectra, written in the programming language Python. The routine was extended to account for spin-polarised systems and can be further modified for own purposes. The concepts and algorithms implemented in SpecProFi are currently being ported to Python, integrating our own simulation routines. We intend to finally provide a user-friendly open-source GUI application for EPR data processing and elaborated data analysis.

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How to make the most of π pulses: dynamical decoupling of nitroxides

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Decoherence determines resolution. For this reason, the understanding and manipulation of transverse electron spin relaxation is pivotal for pulsed EPR experiments. Spectroscopic manipulation by repeated refocusing suppresses spin coherence decay. Carr and Purcell established this concept already in the 1950s [1]. During the last two decades, the quantum information community resumed this working principle, coining the term dynamical decoupling (DD). These efforts included the introduction of an optimized pulse scheme by Uhrig [2].

Here we show how to make most of n π refocusing pulses for nitroxides in *o*-terphenyl, taking into consideration temperature, deuteration and concentration effects [3]. We chose *o*-terphenyl as a well-studied glass former because of its lack of specific interactions with the solute molecule. Based on the transverse relaxation of our model systems under the Hahn echo experiment ($n = 1$), we define distinct temperature regimes. At low temperatures, we observe two separable relaxation contributions with a fast (T_{m1}) and a slow (T_{m2}) phase memory time. Our choice of sample composition identifies these as molecule- and matrix dependent (Figure 1a). At 40 K, T_{m1} and in particular T_{m2} are prolonged by 2 to 5 refocusing pulses, while the matrix nuclei determine the superior DD performance of either the Carr-Purcell or Uhrig scheme (Figure 1b). At elevated temperatures (80 K or room temperature), DD does not preserve electron spin coherence, independent of the sample composition, as (intra)molecular motion dominates relaxation.

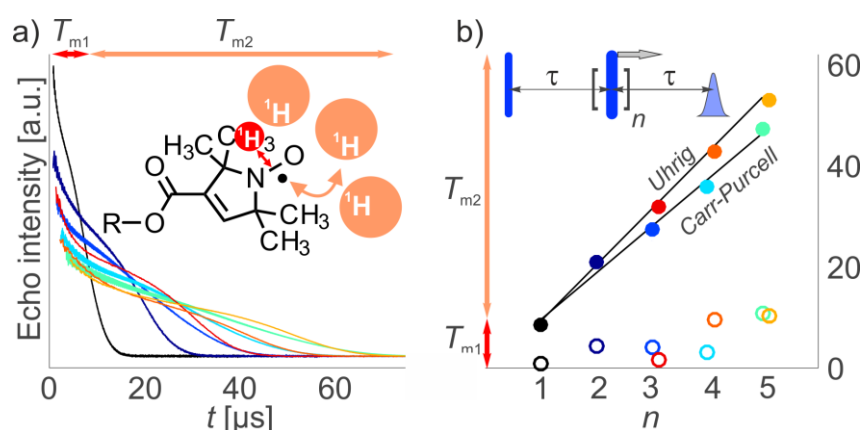


Figure 1: a) Relaxation traces of the displayed nitroxide in *o*-terphenyl (20 μM , 40 K) under Carr-Purcell and Uhrig DD schemes for $n = 1$ to 5 π refocusing pulses. b) Associated T_{m1} (empty) and T_{m2} (filled) phase memory times.

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Poster Abstracts



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EPSRC National UK EPR Facility and Service



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The University of Manchester hosts the EPSRC National EPR Research Facility and Service, that accommodate several Bruker EPR instruments, allowing CW and pulsed EPR measurements at frequencies between 1 (L-band) and 95 GHz (W-band), and a SQUID magnetometer. Together these make a unique research base for studying various types of paramagnetic species and materials. EPR is of wide application in chemistry, physics, materials, biology and medicine.

The Facility has state-of-the-art experimental techniques for multi-frequency EPR and data modelling, including:

- Continuous wave (CW) EPR at 1, 4, 9, 24 and 34 GHz frequencies (L-, S-, X-, K- and Q-band), with optical and electrochemical “pump-probe” methods.
- Pulsed EPR at 4, 9 and 34 GHz, for ESEEM, ENDOR, ELDOR and HYSCORE methods.
- Collaborative arrangements at Oxford University for CW and pulsed EPR at 94 GHz.
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High field pulse EPR for structural studies of CCR4-NOT nuclease complex.

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We are aiming to develop a technique for producing structural models of protein complexes, with known structures of individual subunits but unknown overall complex structure. Our approach combines a) attaching spin-labels at defined sites in the protein of interest, b) measurements of distances between those labels in a complex using pulse EPR and c) computational molecular modelling using thus obtained distances, to produce a full structural model of a complex. We aim to lay a groundwork for studies of CCR4-NOT – a multisubunit protein complex playing an important role in gene regulation. Here we show the feasibility of the elements of this approach.

To demonstrate the sensitivity of distance measurements using a homebuilt W-band pulse EPR machine at UoN we have measured a distance between a pair of Mn^{2+} centers in the nuclease domains of BTG2-Caf1-CCR4 tri-molecular complex (part of CCR4-NOT system). RIDME experiment reveals a Mn^{2+} - Mn^{2+} distance of 6.4 ± 0.5 nm in a sample with a protein concentration below 0.1 mM and an overall volume of 2-3 μl .

We investigated the feasibility of producing protein complex models using molecular docking software HADDOCK and mock EPR data. The nitroxide spin labels were computationally attached using MMM software (Y. Polyhach et al., PCCP 2010) to individual subunits of a bimolecular complex, consisting of NOT1 MIF4G domain co-crystallized with Caf1. The distance distributions obtained using rotamer libraries were used as restraints for molecular docking calculations in HADDOCK with two subunits of the bimolecular complex as a starting material. The model resulting from such calculations is in perfect agreement with its X-ray structure, thus demonstrating the plausibility of an approach with real EPR distance measurements data.





Trityl tags for W-band distance measurements in proteins

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Pulsed Dipolar Electron Paramagnetic Resonance (PD-EPR) combined with Site-Directed Spin Labelling (SDSL) is a valuable tool in structural biology in measuring distances (2-10 nm) between specific sites in biomolecules. PD-EPR can also be applied in the intracellular environment using reductively stable tags. Gd^{III} [1] has so far shown the best in-cell performance, though trityl [2] and specially designed nitroxides [3] can work as well. Here, we present the *in vitro* performance of the CT02-MA trityl spin label for W-band Double Electron-Electron Resonance (DEER) on two proteins; the D39C-E64C mutant of ubiquitin and the T11C-V21C mutant of GB1 protein. This spin label features a thioether conjugation to the protein that is stable in the cell. We optimized the experimental conditions for measuring trityl-trityl distances using rectangular and chirp [4] pulses. We, then, compared the results to those obtained with the same proteins labeled with the Gd^{III} tag DO3MA-3BrPy that has been shown to be suitable for in cell PD-EPR. [1b] Trityl radicals were found suitable for in vitro applications at W-band, however exhibiting poorer sensitivity when compared to DO3MA-3BrPy, most probably due to the lower labeling efficiency. Distance measurements on GB1 at various field positions revealed no orientation selection, unlike earlier reports on oligoDNAs which are probably more rigid than our proteins. [5] We also carried out Double Quantum Coherence (DQC) measurements but the sensitivity was considerably lower than the W-band DEER. Overall, we demonstrate for the first time the feasibility of performing in reasonable times W-band trityl-trityl distance measurements in two proteins.

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A Gadolinium EPR Label for Selective Protein Conjugation: Minimising the Zero-field Splitting and the Tether Length

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We report a novel gadolinium(III)-spin label complex, exhibiting a small zero field splitting, with the ability to tether to the natural amino acid cysteine via a single bond. Here, we demonstrate its potential as a protein spin label by selective labelling of both a test peptide and protein. Importantly, we show the application of this new gadolinium(III) spin label to double electron electron resonance (DEER) by measuring the nanometre distance between a pair of the gadolinium labels, in addition to the distance between the gadolinium label and MTSL, on TRIM25. The label offers high labelling efficiency and promising relaxation times at Q-band, allowing for long DEER measurement time windows. This complements its narrow zero field splitting which has been shown to suit longer interspin distances [1].

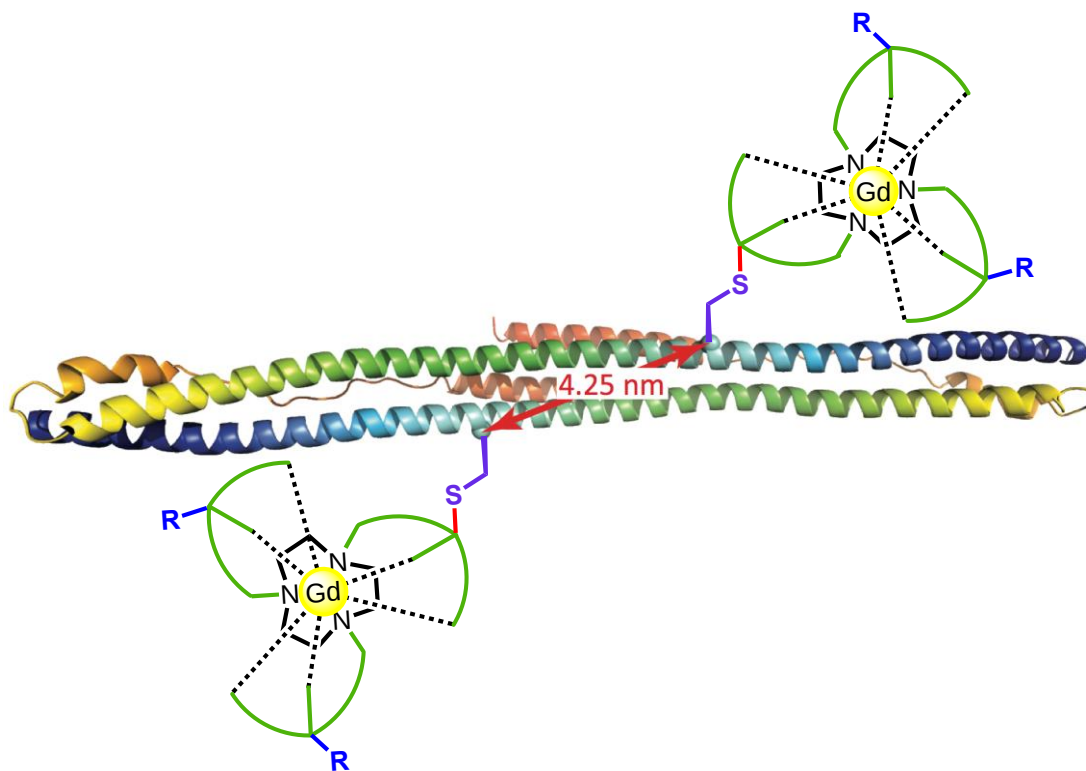


Figure 2: TRIM25 R236C dimer (4ltb.pdb) labelled with the novel gadolinium(III) label with an expected distance of 4.25 nm between the alpha carbon of the cysteines.

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Insights into histidine-rich glycoprotein from electron paramagnetic resonance spectroscopy

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Histidine-rich glycoprotein (HRG) is a mammalian glycoprotein of approximately 70 kDa [1]. It is highly abundant in blood plasma (at low micromolar concentrations) and known to play a role in a variety of biological processes, such as coagulation, angiogenesis, or immune complex clearance, which brought the protein the nickname ‘Swiss army knife’ of mammalian plasma [1-3]. The protein consists of several domains, including a histidine-rich region (HRR), and can bind to a range of different metal ions or ligands thought to influence (or direct) the biological function [2, 4]. Zn^{II} has been shown to bind to the HRR and alter the affinity of HRG for other targets. The stoichiometry of the interaction between divalent metal ions and HRG ranges from between 1 to 10 equivalents up to 18 to 22 equivalents in the literature [2, 5, 6]. In this study, we investigate binding of divalent cations to HRG using electron paramagnetic resonance (EPR) spectroscopy. Instead of using the diamagnetic Zn^{II} the EPR-active paramagnetic Cu^{II} is employed. Two different pulse EPR techniques suitable for distance determination are compared, the well-established pulsed electron-electron double resonance (PELDOR) technique, and the emerging relaxation-induced dipolar modulation enhancement (RIDME) technique. Modulation depths for both techniques are quantitatively assessed for an HRG-Cu pseudo-titration series, comparing different samples where the amount/concentration of protein is kept constant and increasing equivalents of Cu^{II} are added. Data show a saturation with Cu^{II} at a stoichiometry of ~1:12 HRG: Cu^{II}, which is consistent with recent isothermal titration calorimetric data [5]. Distance distributions are broad indicating either a flexible protein leading to a broad distribution of Cu^{II}-Cu^{II} distances or that numerous binding sites are equally populated. We further investigated continuous wave EPR spectra and Election Spin Echo Envelope Modulation (ESEEM) experiments to conclude that binding sites are most likely equally populated even at low Cu^{II} loading levels. This finding is consistent with a structural transition induced by Zn^{II} binding at locally elevated concentration (*e.g.* during tissue damage).

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Pulsed Dipolar Spectroscopy exploiting photogenerated triplet states – a model peptide study

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While traditionally pulsed dipolar spectroscopic methods have used permanent spin labels, such as nitroxides, there has been recent interest in using other forms of spin centres including optically excited moieties, such as free base porphyrins [1].

Two different methodologies to measure systems containing a nitroxide (NO) centre and a photogenerated triplet state of a porphyrin moiety have been reported: The first uses Double Electron-Electron Resonance (DEER): here photogeneration of the triplet (detection spin) precedes the usual DEER sequence in which the stable nitroxide spin serves as the pump spin [1]. The second method, Laser-Induced Magnetic Dipole spectroscopy (LaserIMD) detects the nitroxide signal whilst using a time varying laser pulse to generate a triplet, acting as a pump [2].

In this work we compare the two methods for two peptide systems with inter-spin distances of ca. 2.1 nm and 4.3 nm. Results were recorded at Q-band in a Q TII 3 mm resonator. Photoexcitation was provided by a YAG laser operating at 532 nm.

The modulation depths achieved for the triplet detected DEER and the LaserIMD were 0.15 and 0.03, respectively. The 2.1 nm system required a time trace of ≥ 700 ns to determine accurately the distance distribution [3], and the DEER and the LaserIMD provided traces of similar signal-to-noise. As expected, the 4.3 nm system requires a longer time trace to fully describe the dipolar oscillations. In this case the faster T_m relaxation for the nitroxide, compared to the porphyrin triplet, and the smaller modulation depth of the LaserIMD gives the DEER data the better signal-to-noise for an appropriate time window (see Fig1.).

We also present an extension of the LaserIMD technique by the introduction of a second inversion pulse. As with the analogous extension from usual 3-pulse to 4-pulse DEER, this moves the zero-time from being coincident with a pulse to being coincident with the primary echo of the sequence. This has the advantage of introducing symmetry about the zero-time, and thus allowing a more accurate determination; leading to an improved distance analysis.

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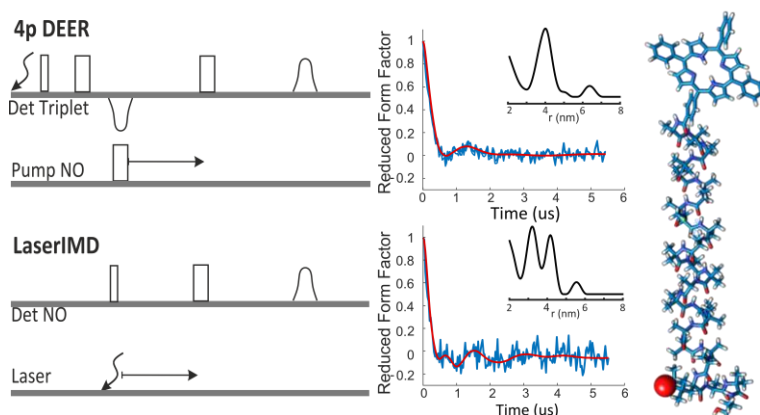


Fig1. Pulse sequences for 4p DEER and LaserIMD with data recorded for the 4.3 nm peptide system, structure shown (NO indicated by red sphere).





Design of an AWG-based Q-band EPR spectrometer system for pulse EPR

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The increased use of arbitrary waveform generators in EPR has prompted the development of a new type of EPR spectrometer centered around an AWG as main signal source and adapted to exploit the new possibilities in pulse sequence design provided by them, in particular wide-band excitation and detection as well as the ability to characterize and correct for distortions caused by hardware components in the signal path [1-3].

At the University of Washington, we are building a Matlab-controlled AWG-based pulse EPR spectrometer based on a microwave bridge designed in collaboration with Millitech (now Smiths Microwave). The aim is to develop a system with a high degree of amplitude and timing precision as well as a high degree of flexibility in instrument control.

The microwave bridge is based on a double up/downconversion design with an instantaneous bandwidth of 1 GHz and a center frequency that can be set from 33.25 to 34.75 GHz. The AWG input in the range from 0.5 to 1 GHz is amplified in the transmitter by a 10 W solid state GaN amplifier. The receiver is characterized by a low noise figure (5.5 dB), while still allowing for efficient receiver protection (>60 dB). Variable amplification and different receiver signal pathways provide a high dynamic range.

The spectrometer control software is designed to allow maximally flexible pulse sequence programming with arbitrary pulse shapes, arbitrary parameter incrementations (linear, non-linear, coupled) and multiple experiment dimensions. The modular design with clear separation of the hardware-specific layer allows for high adaptability to changes in hardware components. The software relies on EasySpin for shaped pulse definitions and compensation for transmitter nonlinearities and resonator bandwidth [4,5].

A system that can be well-characterized in terms of frequency-, amplitude- and phase response of the hardware, combined with software that allows compensation for non-ideal behavior of hardware components and a high degree of freedom in programming pulse EPR experiments will facilitate further developments in the design and application of pulse sequences with precise and quantitative spin control.

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Insights into visible-light activity of g-C₃N₄/TiO₂ nanopowder photocatalysts

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The application of photocatalytic processes in the large-scale remediation of polluted water and air brings demand for the synthesis of non-toxic and cheap photocatalysts with the adequate activity upon UV and visible-light exposure. A great effort was oriented on the synthesis and characterization of metal-oxide-based photocatalytic materials by controlling their morphology, surface modification or doping with metal or non-metal elements. New impulse in the preparation of visible-light active semiconducting photocatalysts represents the discovering of photocatalytic properties of graphitic carbon nitride (g-C₃N₄), a metal-free conjugated polymer consisting of carbon and nitrogen atoms connected *via* tri-s-triazine-based patterns with a band gap energy of 2.7 eV [1]. Despite the fact that the photoinduced activity of g-C₃N₄ is negatively influenced by the limited surface area and rapid recombination processes of photogenerated charge carriers, its combination with a suitable metal-oxide-based photocatalyst, *e.g.* TiO₂, allows to obtain the photocatalytic material active in both spectral regions [2]. The annealing of melamine as g-C₃N₄ precursor and titanium dioxide at high temperature leads to the formation of composite photocatalysts with properties strongly influenced by the initial melamine/TiO₂ loading [2]. The synthesized g-C₃N₄/TiO₂ nanopowders prepared by the annealing of melamine and TiO₂ (P25) at 550 °C were investigated under dark and upon UV or visible-light photoactivation by X- and Q-band cw-EPR spectroscopy. For the photocatalysts synthesized with a lower titania content, the paramagnetic signals characteristic for the g-C₃N₄/TiO₂ nanocomposites were found already before exposure, and attributed to the conduction electrons in the localized π -states in g-C₃N₄ or oxygen vacancies in TiO₂ matrix ($g = 2.003$) along with resonances typical for various Ti(III) centers [3]. The UV or visible-light exposure has negligible effect on the paramagnetic signals of Ti(III) species under given experimental conditions, but the samples annealed using higher TiO₂ loading revealed a photoinduced generation of paramagnetic nitrogen bulk centers ($g_1 = 2.005$, $g_2 = 2.004$, $g_3 = 2.003$ and $A_{N1} = 0.23$ mT, $A_{N2} = 0.44$ mT, $A_{N3} = 3.23$ mT) typical for N-doped TiO₂. The response to visible light regarding the paramagnetic species generation ($g > 1.99$) in studied samples at 100 K was significantly more intense in comparison to UV exposure and a substantial increase was found for samples with the structure representing N-doped TiO₂.

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Structural Characterization of low-coordinated Ti(III) alkyl species by Pulsed EPR Spectroscopy

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Low-valent Titanium(III) alkyl species have been proposed as possible key reaction intermediates in important industrial processes, such as Ziegler-Natta heterogeneous catalysis [1], an ethylene polymerization reaction which in spite of its widespread application remains poorly understood. Previous studies on Ti-based Ziegler Natta catalysts have shown multiple Ti(III) sites in active catalysts, including surface-exposed sites suggested to be active centers for catalysis [2]. Accurate structural characterization in this complex mixture of different Ti centers remains challenging.

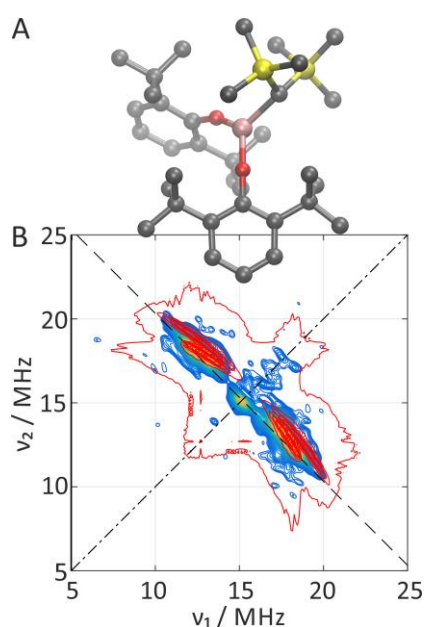


Fig. 1 Ti(III) alkyl model complex.
A Structure of $(\text{ArO})_2\text{Ti}[\text{CH}(\text{TMS})_2]$.
B HYSCORE spectrum, ^1H region.

Here, we address this problem via synthesis and characterization of well-defined, soluble, low-valent Ti(III) alkyl model complexes. These allow us to benchmark the spectroscopic toolkit of modern pulsed EPR-based hyperfine spectroscopy. Starting from a combination of HYSORE spectroscopy [3] and DFT calculations on structures obtained by X-ray crystallography, we demonstrate the identification of nuclei, e.g. ^1H or ^{13}C , with couplings indicative of the Ti(III) environment for model complexes, such as $(\text{ArO})_2\text{Ti}[\text{CH}(\text{TMS})_2]$ (Fig. 1). The experimental hyperfine couplings are found to be in good agreement with DFT predictions and hence are shown to serve as diagnostic features of the structure of the molecular Ti(III) complexes. Comparing these to hyperfine couplings obtained from surface-bound Ti(III) species that are catalytically active in ethylene polymerization allows to characterize the local structure in an environment that is barely accessible by other techniques. That way potential intermediates can be identified that are responsible for catalytic activity.

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EMR of photovoltaic non-fullerene acceptor polymer blends

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Organic photovoltaic (OPV) devices are dominantly based on the bulk heterojunction architecture, a donor polymer blended with an electron accepting fullerene. The development of new donor polymers has enabled advances in OPV cell efficiencies. However, the search for alternatives to the methanofullerene derivative acceptors, which exhibit excellent electron transporting properties, has proved more challenging. Recently, non-fullerene acceptors have been developed which when incorporated into OPV cells are achieving comparable efficiencies. Electron magnetic resonance (EMR) methods provide unique characterisation of negative polaron states localised on the acceptors. Here we report EMR studies on two high performance non-fullerene acceptors, 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) (Fig. 1) and EH-IDTBR which has a indacenodithiophene (IDT) core alkylated with branched 2-ethylhexyl, blended with the widely used donor polymer Poly-3-hexyl thiophene (P3HT).

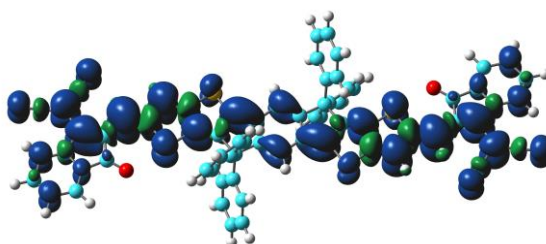


Figure 1 ORCA spin density representation of the negative polaron on the ITIC core.

Light-induced field-swept pulsed EPR measurements were performed at 9.8 GHz, 34 GHz, and 94 GHz and the spin-Hamiltonian parameters for the negative polaron on ITIC and EH-IDTBR were obtained. Davis ENDOR spectra were measured at 9.8 GHz and 34 GHz. Density functional theory calculated g-values and proton hyperfine tensor values were obtained using ORCA and are also reported.





EPR of Fe^{3+} -centres in ferroic titanate oxides

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EPR of Fe^{3+} centres in SrTiO_3 enabled the first structure determination of the low temperature antiferrodistortive phase, it subsequently provided a measure of the order parameter for this phase transition and provided detailed insight on its nature. In addition, the identification of both the $\text{Fe}_{\text{Ti}}^{3+}$ centre, where the ion substitutes in a fully coordinated oxygen octahedron, and $\text{Fe}_{\text{Ti}}^{3+} - \text{V}_{\text{O}}$ centre, where charge compensating nearest neighbour oxygen vacancy occurs, have led to the development of a clear understanding of the defect physics and chemistry of these materials. This knowledge is routinely used to inform the engineering of improved electronic and ferroic material properties. Strontium titanate at room temperature is a model cubic perovskite, there is no ferroelectric displacement. In contrast to the commercially relevant ferroelectrics BaTiO_3 and PbTiO_3 , which exhibit a tetragonal distortion. The fourth order zero field splitting (ZFS) terms dominate for $\text{Fe}_{\text{Ti}}^{3+}$ in SrTiO_3 , but also make notable contributions to the spectra of the $\text{Fe}_{\text{Ti}}^{3+} - \text{V}_{\text{O}}$ centres. However, despite the extensive studies of this system unambiguous values for the fourth order terms are still lacking for the $\text{Fe}_{\text{Ti}}^{3+} - \text{V}_{\text{O}}$ centre.

Here we report single crystal EPR measurements on Fe^{3+} centres SrTiO_3 and BaTiO_3 and obtain accurate 2nd and 4th order ZFS terms. These are compared to the known ZFS terms for Fe^{3+} centres PbTiO_3 [1]. The relation between the ZFS terms and the local structure of the defect centres for the three perovskite titanate oxides are discussed with the aid of Newman superposition model calculations.

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EPR and UV-vis-NIR spectroelectrochemistry of five-coordinate manganese(III) complex with a salen type ligand, a catalyst of secondary alcohol oxidation

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The manganese(III) ion is ubiquitous among chemical systems that exhibit fascinating biological and physical properties, ranging from photosystem II and ribonucleotide reductase to the renowned single-molecule magnet Mn₁₂. The studied complex [MnL(NCS)]·0.4H₂O (**1**) was prepared by reaction of previously synthesized complex [MnL(OAc)]·0.15H₂O [**1**] with KSCN in methanol [2]. These closely related systems with noninnocent tetradentate Schiff base ligand were found to act as catalysts or catalyst precursors for the oxidation of some secondary alcohols to ketones.

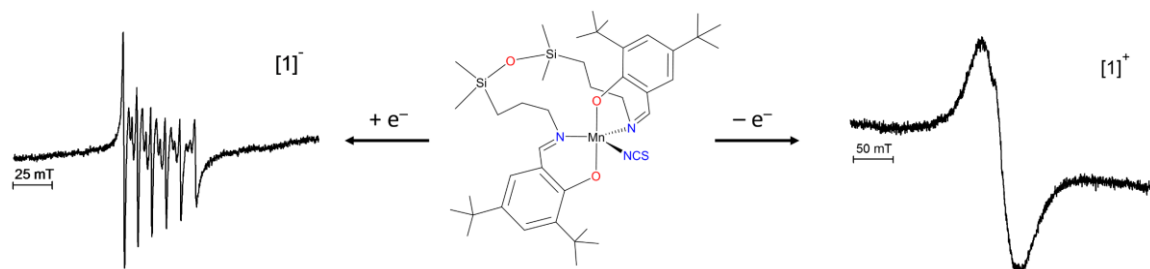


Figure 1. The investigated complex MnL(NCS) (**1**) and X-band EPR spectra of electrochemically generated [**1**]^{•-} and [**1**]^{•+} in dichloromethane/nBu₄NPF₆ measured at 120 K.

Irreversible or quasi-reversible redox behaviour was observed in both cathodic and anodic region. To confirm the chemical reversibility of the first reduction as well as the first oxidation step of complex **1**, the in situ spectroelectrochemical UV-vis-NIR and cyclic voltammetric experiments were carried out under an argon atmosphere in a thin layer cell. By decreasing the voltammetric scan rate, the cathodic reduction becomes more electrochemically reversible, confirming a slow electron transfer mechanism at this step. To investigate the electronic structure and spin state of the reduced and oxidized MnL(SCN), ex situ EPR experiments were performed after one electron transfer (Figure 1). X-band EPR spectra recorded in frozen dichloromethane solutions of [**1**]^{•-} indicated reduction to a Mn^{II} species, whilst the one-electron oxidized state [**1**]^{•+} can be tentatively assigned to a Mn^{IV} species. The shape and splitting of the corresponding EPR spectra strongly depend on the temperature and the sample concentration. Quantum chemical calculations confirmed the reduction of Mn^{III} to Mn^{II}, but suggested that the oxidation is a ligand centered process.

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Phase segregation in transition metal (Co^{2+} , Mn^{2+}) doped lead halide perovskites from solid-state NMR

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Lead halide perovskites attract growing interest owing to their highly tunable optoelectronic properties. Mn^{2+} doping is a firmly established way of enhancing luminescence yield in all-inorganic CsPbX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) perovskites for high performance light-emitting diodes.[1-3] Co^{2+} doping has recently been reported as a viable way of tailoring the photovoltaic properties of methylammonium lead iodide (MAPbI_3).[4] However, until now the atomic-level picture of lead replacement in these materials has been missing. Since incorporation of transition metals into a diamagnetic perovskite lattice should lead to paramagnetic relaxation enhancements (PREs), nuclear relaxation is expected to be a sensitive probe of transition metal substitution.[5] Here, using ^1H and ^{133}Cs solid-state MAS NMR relaxation measurements at 21.1 and 9.4 T, and CW EPR, we show that, contrary to current conviction, Co^{2+} does not replace Pb^{2+} in MAPbI_3 . Similarly, we provide the first atomic-level evidence that Mn^{2+} forms $\text{CsPb}_{1-x}\text{Mn}_x\text{X}_3$ alloys.

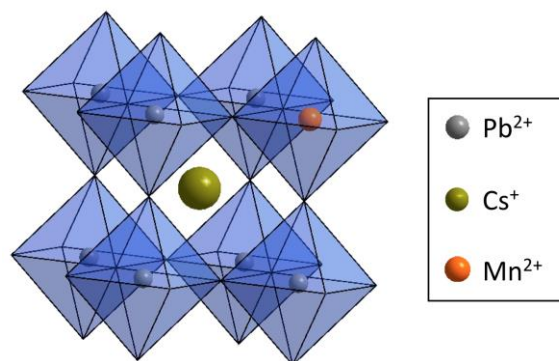


Figure 1. Schematic representation of CsPbX_3 doped with Mn^{2+} . Each edge of an octahedron contains an X^- anion.

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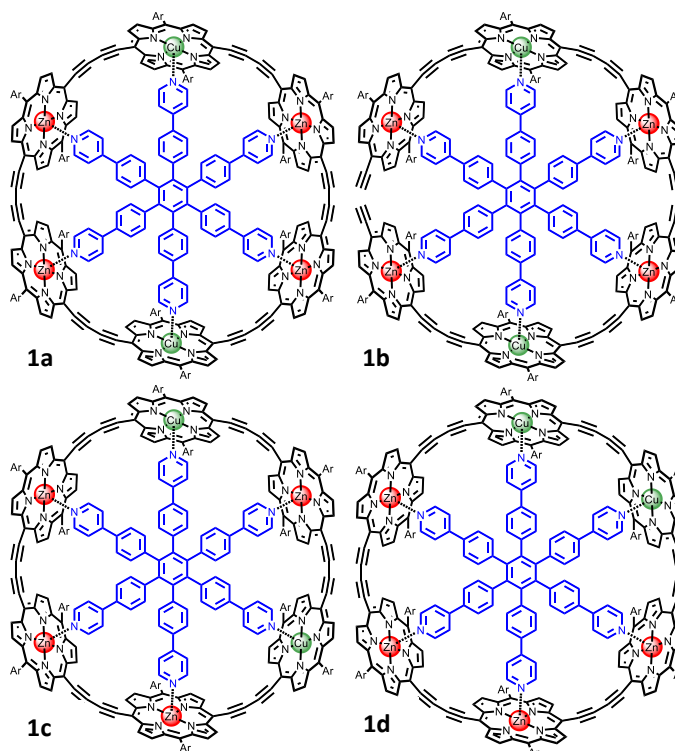
Investigations into Quantum Interference Phenomena in Supramolecular Assemblies Using Pulsed Dipolar Spectroscopy

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Significant through-bond exchange interactions (J) between two spin centres can manifest in the results of EPR Pulsed Dipolar Spectroscopies (PDS) such as DEER and RIDME, which are more commonly used to measure through-space dipolar interactions (D) [1]. Recently, DEER was used to measure the exchange interaction between two Cu centres in a six-membered porphyrin nanoring [2]. The system containing two conjugated linkers (**1a**) was found to have J coupling 4.5 times stronger than the system in which a pathway was removed by cutting one of the conjugated linkers (**1b**), an observation indicative of constructive quantum interference between the spins [2][3].



Here we develop a geometric model based on measurements taken on a system analogous to **1b** in which both linkers are cut and therefore no exchange coupling is present. This model is then used to predict the dipolar coupling present in systems that connect the spins via non-identical linkers - with the coppers arranged in *meta* and *ortho* orientations (**1c** and **1d** respectively) - allowing J coupling contributions in the PDS traces to be investigated.

We find that the size and distribution of the J couplings present is influenced by the structural rigidity of the systems. This is demonstrated by altering the number of template legs, and also by removing the template completely. Furthermore, the nature of the central diamagnetic metal ions in the linker porphyrins affects the magnitude of the exchange interaction significantly. This specificity of control affords interesting possibilities for using these systems in molecular electronics.

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Characterization of Spin Dynamics in Open-Shell Aromatic Radicals through EPR spectroscopy

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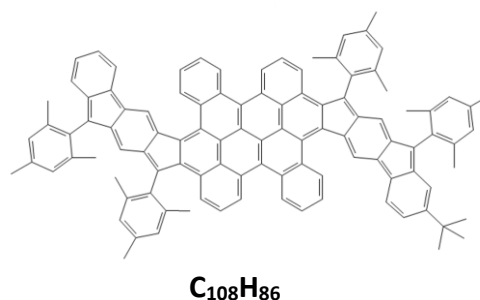
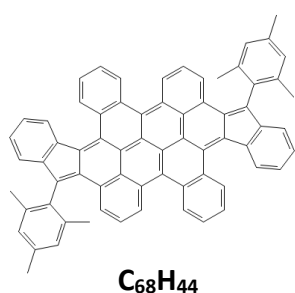
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Polycyclic aromatic hydrocarbons (PAHs) are a series of compounds that have attracted a great deal of interest for their semiconducting properties. Recently, it was possible to synthesize open-shell stable compounds [1]. These radicals are very promising because they allow spin manipulation in an environment with very low nuclear coupling. In addition to this, it was demonstrated that their characteristic as radicals depend on their conjugation length and on their shape. Particularly, they strongly relate to graphene nanoribbons, since the topology determines their magnetic properties [2]. We introduce the study of two open-shell radicals. The synthetic strategy is based on incorporating two diindeno groups on a bishrysene scaffold, obtaining a shape with coved edges as shown in the figure [3].

We performed EPR characterization of the two compounds in the solid state and in deuterated toluene solution. The variable temperature CW signal revealed the separation between the triplet and the singlet state. The measurement of T_1 with temperature highlighted different mechanisms for spin-lattice relaxation, especially a direct process at low temperature and a Raman process at intermediate temperature. The T_2 resulted flat around 100 ns below 10 K and quickly decaying at higher temperature. The envelope modulation of the spin-spin relaxation time will be treated to obtain the main decoherence paths.

In future work, we propose to use Double Electron-Electron Resonance (DEER) to resolve the spin-spin interaction. In addition to this, owing to the small band gap, excited states can be easily accessed with near IR laser excitation. Therefore, we suggest to use Transient EPR (TrEPR) to probe the spin dynamics of the excited levels.



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Broadband excitation for distance measurements between Cu(II) centers

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Technological advances in the last years enabled by Arbitrary Waveform Generators (AWGs) provide access to broadband excitation by frequency-swept pulses. At Q band, this was so far mainly exploited to enhance the sensitivity of distance measurements of high-spin systems, e.g. Gd(III) [1]. Here, we explore the potential gain and the current limitations for broadband measurements of spin $S = \frac{1}{2}$ systems at Q band. In this case, high-spin effects are absent. Metalloproteins with broad spectra, as for example Cu(II)-containing systems, are naturally abundant and a highly interesting class of samples for dipolar EPR spectroscopy [2]. Without frequency-swept excitation, sensitive distance measurements for such systems were difficult up to now.

The bandwidth limitation imposed by the resonator ultimately limits the increase in excitation bandwidth that can be achieved by instrument development. We show how this problem can be addressed with high-bandwidth Q-band resonators developed recently in our laboratory [3]. The resonating structures are loop-gap designs with multiple gaps on which the E field is symmetrically distributed. Strong and homogeneous B_1 fields are achieved. The bandwidth can be varied by adjusting the position of a coupling rod. In the broadest setting, 12 ns π pulses are possible over a range of nearly one GHz.

For a bis-Cu(II) ruler compound, Double Electron Electron Resonance (DEER) measurements at Q band using the broadband resonators are explored. They are compared to X-band measurements performed with a widely used commercial MS3 split-ring resonator (Bruker). The broad bandwidth of the homebuilt loop-gap resonators allows to exploit the order of magnitude higher sensitivity at Q band, while a considerable fraction of the spectrum can be excited within one measurement. Orientation selection effects observed in Cu(II) broadband DEER are compared to the same effects in Relaxation-induced Dipolar Modulation Enhancement (RIDME) experiments. The gain in DEER sensitivity by the use of shaped pulses for the pump as well as for the observer pulses is assessed.

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Transient EPR study of the photo-excited triplet state of a series of linear palladium (II) porphyrin oligomers

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Porphyrin oligomers form part of a myriad of π -conjugated organic molecules proposed for applications such as molecular wires, artificial energy conversion devices, and nonlinear optical materials [1]. The triplet state delocalisation in linear butadiyne-linked Zn^{2+} /free-base porphyrin oligomers (ZnP_n/P_n) has previously been investigated by studying the zero-field splitting (ZFS) interaction and the $^1\text{H}/^{14}\text{N}$ hyperfine couplings as a function of oligomer chain length, n [2]. One of the limitations of investigating the extent of triplet state delocalisation on these systems is that as n increases beyond 3 or 4, the EPR signals become progressively weaker due to a decrease in triplet yield, thus making measurements with sufficient signal-to-noise for oligomers with $n \geq 6$ difficult and time-consuming.

In this work, we attempt to increase the triplet yield by replacing the Zn^{2+} with Pd^{2+} which, by virtue of its larger atomic number, drives the triplet formation predominantly via a direct spin-orbit coupling (SOC) mechanism [3]. Although the lifetime of the triplets is short as compared to the Zn^{2+} analogues (as triplet decay is also driven by SOC), the triplet yield is larger in the Pd^{2+} analogues and the EPR signals remain strong throughout the series $n = 1-7$.

The increased SOC interaction due to Pd^{2+} ($S=0$, $4d^8$, square planar coordination) is also expected to influence the ZFS ($\mathbf{D}_{\text{SOC}}$ contribution) and g -values observed in the EPR spectrum as compared to Zn^{2+} . This is confirmed by the fact that the absolute values of the ZFS parameters in the Pd^{2+} series are larger by a factor of two as compared to the Zn^{2+} series, and by the observation of an axial g -tensor in Pd^{2+} (cf. isotropic g for Zn^{2+}).

Magneto-photo-selection and ENDOR experiments also demonstrate that the Z -axis of the ZFS tensor lies in the plane of the porphyrin chain for the entire Pd^{2+} series. In the case of the Zn^{2+} series, where the spin-spin dipolar interaction of the two electrons comprising the triplet provides the only contribution to the ZFS ($\mathbf{D}_{\text{SS}}$), the Z -axis of the ZFS changes from being perpendicular to the porphyrin plane in the monomer to being parallel to the porphyrin chain in the longer oligomers.

As there is currently no clear theoretical method for accurately and simultaneously describing both contributions to the ZFS tensor ($\mathbf{D}_{\text{SS}}$ and $\mathbf{D}_{\text{SOC}}$), this work aims to characterise experimentally the ZFS of the PdP_n series and reproduce the experimental trends by means of CASSCF calculations. These calculations are key in establishing whether information about the extent of triplet delocalisation can be deduced from the ZFS of systems with non-negligible SOC interactions.

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Identification of radicals formed during the riboflavin/UV-A-induced collagen crosslinking for the treatment of keratoconus

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Keratoconus is corneal ectasia characterized by lesions at every corneal layer with a diagnosis relatively easy to establish using specific examination (keratometry, corneal topography, pachymetry), with a frequency of 1 in 2000 persons [1]. Keratoconus is a non-curable disease, but its evolution can be stopped by different treatments. One of these consists in applying a topical dose of riboflavin drops to the cornea which is exposed to a low amount of UVA light. In this way are formed reactive oxygen species which can determine cross-linking of collagen fibers (Fig 1). This will contribute to corneal strength and its integrity.

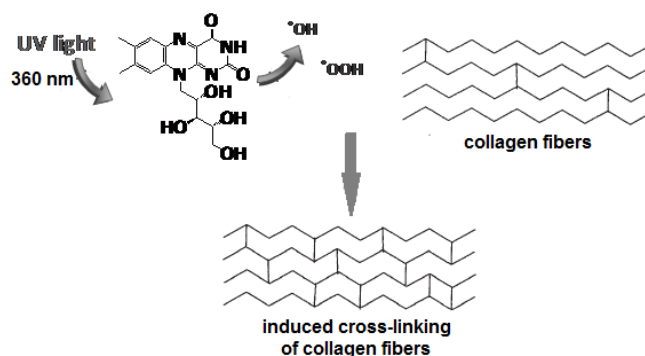


Fig.1: Schematic representation of riboflavin/UVA cross-linking process

The aim of our study was to identify the reactive oxygen species that are formed during exposure to UVA light by analysis of tear secretion collected immediately after the procedure afore mentioned. The following spin traps DMPO, TEMP, CPH were used in order to prove formation of $\text{HO}^\bullet$, singlet oxygen or $\text{HOO}^\bullet$ radicals. The results were correlated with keratoconus stadium for each patient. Moreover, we investigated the formation of ROS in model systems for tears and hyaluronic based drops exposed to UVA light in the presence of riboflavin.

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Radical geometry: a key to efficient Dynamic Nuclear Polarization.

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Dynamic nuclear polarization (DNP) is becoming an essential tool to dramatically improve the sensitivity of numerous experiments in nuclear magnetic resonance (NMR) like the elucidation of surface structure of advanced materials¹ and the characterisation of polymorphs in organic solids². The method is based on the transfer of polarization from electrons to nuclear

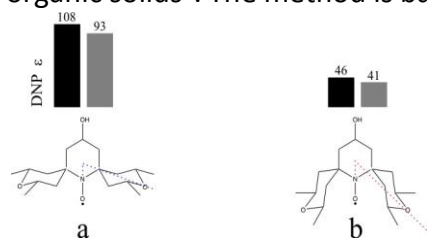


Fig. 1: Nitroxide monoradicals used as polarizing agents for MAS ssDNP experiments at 9.4T, ~100 K, MAS=8000 Hz. The displacement of the cyclohexane sidearms from the nitroxide axis is larger for the open than for the closed configuration (panel a) and b) respectively). The rectangles indicate the MAS ssDNP

spins by saturation of the electron spin transitions. The upper limit of transferable polarization, at equilibrium, is about 660 for ¹H and even more for other low abundant nuclei such as ¹³C, ¹⁵N. The primary parameter to perform an efficient DNP experiment remains by far the choice of the radical³. Several factors have been identified to affect the efficiency of the polarising agent: rigidity, bulkiness, relaxation properties. Here we show for a set of nitroxide mono- and bi-radicals how the local geometric conformation, especially in the vicinity of the unpaired electron spin, leads to considerably different enhancement factors for MAS ssDNP (Magic Angle Spinning solid state DNP) experiments conducted at 9.4 T and ~100K in 1,1,2,2-tetrachloroethane (TCE), glycerol-d₈:D₂O:H₂O, and DMSO-d₆:D₂O:H₂O. We include the local geometry among the set of important variables to consider in the design of new polarising species. The *open* configuration (Fig 1a) leads always to a better DNP enhancement either for the nitroxides mono- and bi-radicals irrespective of the solvent used.

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What do we mean by g-factor in exchange coupled electron spin systems?

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The electron spin resonance (ESR) of spin systems dominated by exchange often exhibits a rather narrow single Lorentzian line. Examples are the ESR of micrometer sized lithium metal particles in LiF, the ESR of graphene like structures in carbon fibres or the conduction electron ESR in β -Ga₂O₃. Due to the exchange narrowing, the line widths at low temperature are in the range of 0.1 Gauß to 0.4 Gauß. The g-factors can be very near to $g = g_{\text{free}} = 2.002319$ (Li: $g_{\text{free}} \cdot (1+13 \text{ ppm})$, carbon fibre: $g_{\text{free}} \cdot (1+165 \text{ ppm})$) or differ quite substantially from g_{free} (β -Ga₂O₃: $g \approx 1.96$).

Due to these rather narrow line widths and the rather strong ESR signals, the experimental determination of the g-factor seems straightforward. However, in all these materials, there are line shifts of the ESR due to magnetic susceptibility effects in the tenth ppm range: diamagnetic and paramagnetic contributions, which depend on the size and geometry of the samples. Furthermore, there are dynamic contributions due to the conduction electrons itself (SUSHI-effect) and contributions from the unresolved hyperfine coupling to the nuclei (Overhauser shift).

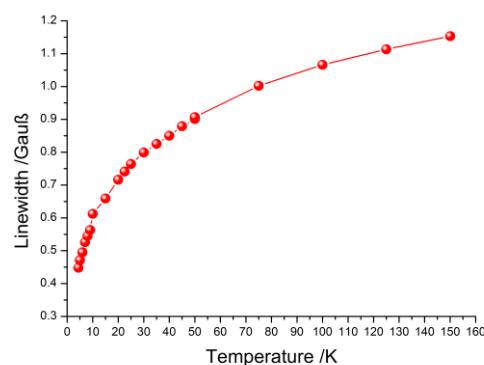


Figure 1. Temperature dependence of the Lorentzian line width in a carbon fibre.

Using the internal nuclei as magnetic field sensors, very precise g-factors can be obtained, as shown in [1]. In order to obtain absolute accuracies below 10 ppm, all of these shift contributions have to be taken into account. We will discuss procedures to determine these contributions and correct them. Furthermore, the "true" Knight shift of the NMR in these materials has to be determined. This can only be done by combined DNP and Overhauser shift double resonance measurements.

These high absolute accuracies are particularly important when using such samples as g-factor standards at high frequencies (W-band or above).

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Using Distance Distribution Information in Integrative Structural Biology

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A large fraction of biomolecules and biomolecular complexes is not amenable to structure determination at atomic resolution with one of the classic approaches of x-ray diffraction, NMR, or cryo-electron microscopy. In many of these cases – and even for some systems that can be engineered to crystallize – an atomic-resolution structure may not even be the right answer, since some extent of disorder is essential for their function. Such systems need to be described by an ensemble of conformations. Distance distributions on the nanometer scale, as they can be obtained by EPR pulsed dipolar spectroscopy (PDS), are extremely valuable for this purpose, as they provide direct information on the width of the ensemble [1]. However, neither the number of restraints that we can obtain by PDS on spin-labelled biomolecules nor their accuracy is sufficient to build models without resort to data from other techniques. This calls for integrative modelling, but existing tools for such modelling are not geared to using distribution information in generating an ensemble.

This is the point of departure for the development of RigiFlex, a module of MMM (<http://www.epr.ethz.ch/software.html>) [2]. RigiFlex applies a divide-and-conquer approach for assembling models from rigid domains and flexible sections of proteins and nucleic acid chains. Rigid-body arrangements (RBAs) can be generated from PDS restraints alone or can additionally take into account cross-link restraints or small-angle scattering curves. An ensemble of RBAs is obtained by an exhaustive scan of solution space and can be analyzed in terms of potential further restraints that could narrow it down. Ensembles of flexible peptide linkers are generated by an approach described previously [3], while modeling of RNA is based on a backbone fragment library [4] and can also use Rosetta-generated fragment libraries [5,6] available via the ROSIE server (http://rosie.rosettacommons.org/rna_denovo).

Here we discuss the concept of structure modeling by integration of several specialist software tools, the divide-and-conquer approach, and exhaustive scanning of RBA solution space by a distance geometry approach. On the example of the complex of the heterogeneous nuclear ribonucleoprotein PTBP1 with an internal ribosome entry site (IRES) section of Encephalomyocarditis Virus we show the utility of RigiFlex in iterative restraint generation by generating ensemble models from incomplete restraint sets. We discuss the current limitations of PDS that should be overcome to make such integrative modelling of large biomolecular complexes from distance distribution restraints more generally applicable.

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Orientation-Selective RIDME with Cu(II)-Nitroxide Spin Pairs using Chirped Pulses

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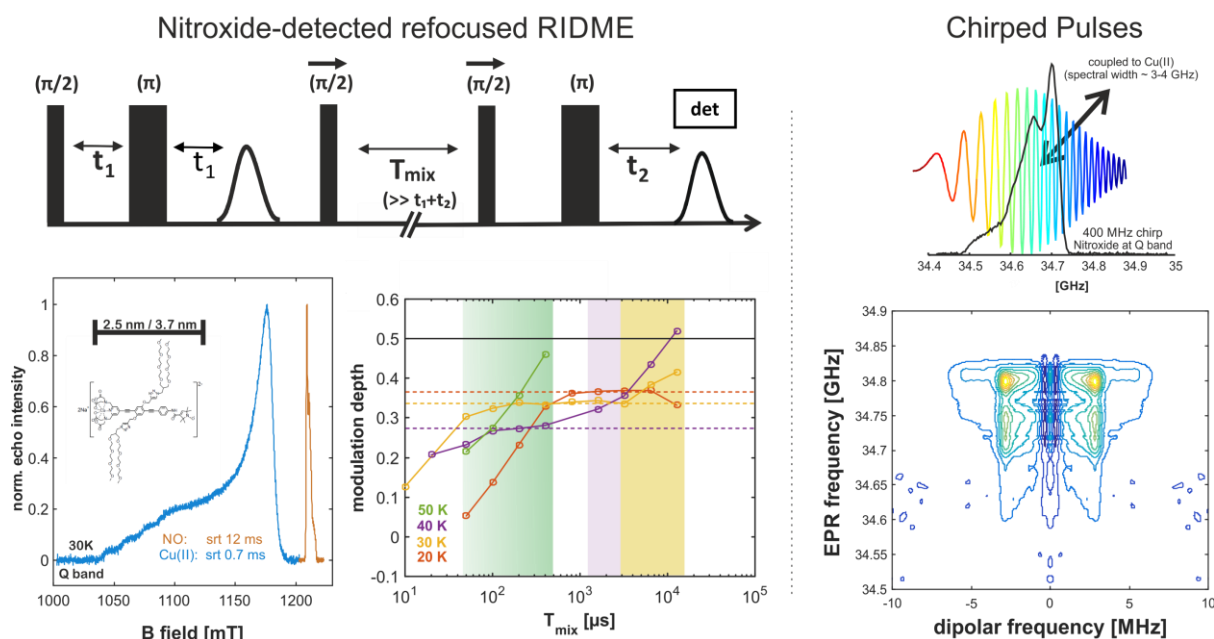
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Pulsed dipolar spectroscopy in metal ion-nitroxide spin pairs has recently seen a surge in method development towards applications in both materials science and biophysical studies. The currently still dominating technique for distance measurements in Cu(II)-nitroxide spin pairs is the two-frequency DEER experiment (also known as PELDOR), but the single-frequency RIDME experiment is an emerging alternative with the potential for increased sensitivity (1–3). Synthesis of water-soluble compounds with one nitroxide moiety and one Cu(II)-chelating ligand at the ends of a rodlike linker allowed for the systematic screening and optimisation of experimental conditions at Q-band. The narrow distance distributions characteristic for these model compounds are well suited for the identification and elimination of experimental complications, which arise primarily from echo-crossing effects and ESEEM contributions. Furthermore, detecting on nitroxide at Q-band opens the door to orientation-selective dipolar spectroscopy. To this end we show the, to the best of our knowledge, first combination of the RIDME experiment with frequency-swept excitation, which provides a two-dimensional spectrum with a Fourier-transform EPR dimension and an indirect dipolar spectroscopy dimension.

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Photodegradation processes in fullerene-free organic solar cells investigated by Electron Paramagnetic Resonance

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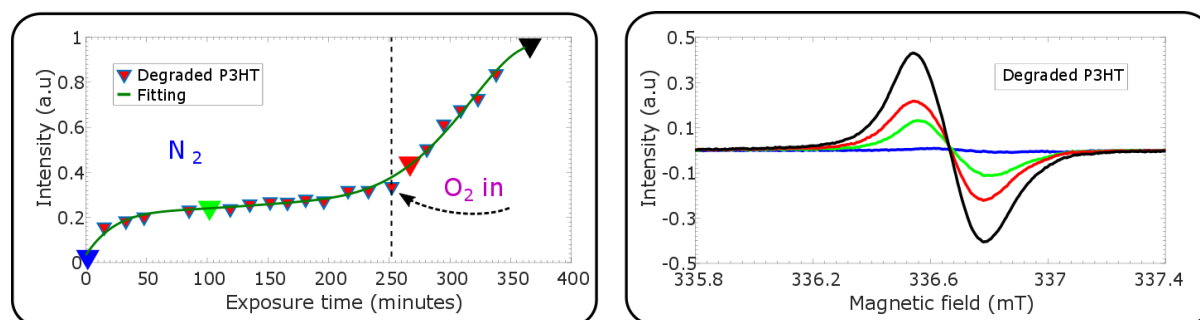
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The constantly growing energy demand and disastrous damage to the environment forces humanity to find a renewable energy source which can be used safely and responsibly. Organic Solar Cells (OSC) can be a suitable technology provided that high efficiencies combined with low fabrication cost and *long lifetimes are in place*. Today, single junction OSCs based on non-fullerene acceptors reach PCE over 13% [1], while efficient roll-to-roll processes for OSCs offering high throughput and low labor costs are already up and running [2].

However, the technology is not yet dominant on the market as the long-term stability under real-life operating conditions remains the main obstacle. The photoactive layer of OSC consist of a nanoscale interpenetrating network of acceptor and donor materials. This layer deteriorates due to several (un)known external factors: oxygen, moisture, light irradiation, mechanical stress and heating [3].

In this work we use multi-frequency (X- and W-band) electron paramagnetic resonance (EPR) as a sensitive and **non-destructive** method to monitor photochemical degradation of a P3HT donor polymer in combination with FBR acceptor molecules under different gas contents. First, the light-induced EPR signal of the positive and negative polarons were characterized in freshly made blends. Next, signals were compared to the EPR spectra observed upon degradation of the pristine materials. While no radical signal could be observed for degraded FBR, clear contributions were found for pristine degraded P3HT.



We found that degradation of the pristine P3HT involves a radical pathway and becomes significant only by combination of light and oxygen. This EPR signal was resolved in two components as previously assigned to positive polaron on P3HT⁺ and negative polaron on [P3HT:O₂]⁻ charge transfer (CT) complex. These features were also observed in degraded P3HT:FBR blends. Light illumination at 20K still revealed CT and associated creation of polarons, necessary for the solar cell application.

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EPR study of ribosomal assemblies. Monte Carlo analysis of DEER data

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Supramolecular ribosomal complexes are responsible for protein synthesis in living organisms. Genetic information provided by messenger RNA is translated into amino acid sequence by the complex involving ribosome and transfer RNAs. As far as conformational changes are highly involved in the regulation of the protein synthesis, the studying of the structural dynamics of ribosome and its ligands is of importance for understanding of the process. Recently, DEER has been employed for determining the structural changes of mRNA analog being a part of ribosomal complexes and for evaluating dynamic properties of ribosomal ligands [1].

In this work [2], to model a structured mRNA, we used a doubly spin-labeled 11-mer RNA UGUGUUCGACA, which bore nitroxide spin labels at the C5 atom of the 5'-terminal uridine and at the C8 atom of the 3'-terminal adenosine. Applying DEER we studied the complexes of a human 80S ribosome with participation of the mRNA, which formed codon-anticodon interactions with tRNAs fixed at ribosomal E, P, A sites.

The measurement of intramolecular distances in the mRNA allowed establishing the fundamental differences between the conformations of the mRNA fixed at ribosomal mRNA-binding site by codon-anticodon interaction with P site-bound tRNA and the mRNA associated with the ribosome in the absence of tRNA. We revealed that the A and E site-bound tRNAs contribute to the stability of the ribosomal complexes. The obtained data allowed making conclusion concerning the absence of the codon-anticodon interaction at the E site.

In order to test the new approach of DEER data processing [3] and verify the considered results we performed multi-Gaussian Monte Carlo analysis in the frequency domain. Calculated distance distributions reveal the same conformations of the mRNA as those obtained by Tikhonov regularization, but feature the peaks having different widths, which leads to a better resolution in several cases [4].

The work was supported by Russian Science Foundation (No 14-14-00922).

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Engineering entanglement in molecular spin systems

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A key advantage of quantum computing over classical computing comes from the phenomenon of superposition, enabling parallel computation. In order to fully exploit its properties, there needs to be a way of controlling the entanglement of the elements of the system. Previously it was shown that in the family of chemically self-assembled double structures of Cr₇Ni spin qubits it is possible to achieve both long coherence times and the control of the inter-qubit quantum interactions. [1] Now, we are designing protocols to use ESR to achieve real entangled states in an ensemble of these dimers, and then demonstrate the entanglement by a density matrix tomography, gaining inspiration from similar procedures realised in NMR quantum computing [2][3]. Unlike nuclear, electronic energy splittings are large enough to produce thermal states of high purity, which should make real entangled, as opposed to pseudo-entangled, states accessible.

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DEER distance measurements with Y@C₈₂ spin labels

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A porphyrin-based receptor for pairs of endohedral fullerenes was designed to bind the fullerenes non-covalently and at a fixed distance as a potential testbed for entanglement operations (figure 1) [1]. Binding of Y@C₈₂ was demonstrated using a variety of methods. Q-band DEER between Y@C₈₂ bound to the receptor, and therefore acting as spin labels, gave distances that aligned with molecular models. The repeating modulations indicated a small distribution of distances. However, X-band DEER was ambiguous since the dipole-dipole modulation frequency overlapped with the ESEEM frequency arising from hyperfine coupling to the Y atom. Despite the successful binding and placing of the endohedral fullerenes, the phase memory time of the Y@C₈₂ dropped rapidly upon binding compared to its value in deuterated toluene alone.

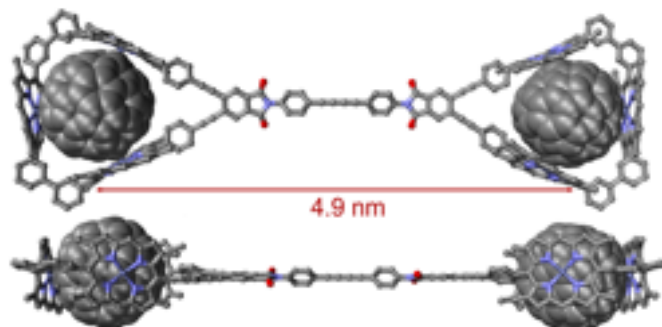


Figure 3: Molecular model of the porphyrin receptor and Y@C₈₂ complex. The red line gives the distance between the centroids of the endohedrofullerenes.

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EPR investigations of ubiquinone reduction by respiratory complex I in native and non-native membrane systems

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Respiratory complex I (NADH:ubiquinone oxidoreductase) is a vital component of the mitochondrial electron transport chain, contributing significantly in establishing the proton gradient necessary for the cellular production of ATP. Oxidation of NADH by ubiquinone is mediated by electron transfer through a chain of 7 Fe-S clusters, generating the energy required for proton translocation. The mechanism by which the electron transfer is coupled to the proton translocation is not yet understood. The binding and reduction of ubiquinone has been heavily implicated in harnessing this redox energy, driving conformational changes which activate the spatially separated proton pumping process [1].

Despite this emerging and important role of ubiquinone in complex I, very little is known about its mechanism of reduction. Though there has been EPR spectroscopic evidence of the formation of semiquinone intermediates, there is little consensus in many of the properties associated with semiquinone radicals. The hydrophobic nature of ubiquinone makes it complicated to study its reaction properties, and native membrane systems suffer from unwanted EPR signal contributions from other respiratory chain enzymes.

Here, we explore the semiquinone signals arising from submitochondrial particles (SMPs) using hyperfine EPR techniques, examining the local environment and investigating their source. Using a chimeric respiratory chain approach, we tentatively assign a semiquinone signal present at low concentration to complex I and establish its hyperfine environment using HYSCORE spectroscopy. We also demonstrate an EPR-optimised proteoliposome system, allowing the study of complex I in a membrane system with its native substrate and defined enzymatic components [2]. We detect a piericidin A sensitive semiquinone signal at low concentrations arising from complex I under turnover conditions with ubiquinone-10. This observation suggests a semiquinone with a low stability constant, agreeing with previous freeze-quench studies on soluble complex I, but not with the extensive data obtained from experiments using SMPs or soluble ubiquinone analogues [3,4]. The absence of a well stabilised semiquinone lends support to a single-stroke mechanism, but further investigations will be required to establish whether semiquinones can be generated under non-equilibrium conditions.

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Dissociation Constant Determination via RIDME Modulation-depth Quantitation

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Pulse EPR has become a popular method for distance measurements on macromolecules. Most commonly, the 4-pulse electron-electron double resonance (PELDOR) [1] experiment is applied to measure between exogenously introduced nitroxide radicals, conjugated to cysteine residues. Information content in PELDOR can be further expanded to include oligomerization-state through quantitation of modulation-depths (Δ) as shown in spin-counting studies. [2]

The emergence of metal labels such as: Mn^{2+} and Cu^{2+} [3-4] to be used as alternatives and in conjunction with nitroxides has driven development of a single frequency technique; the 5-pulse relaxation-induced dipolar modulation enhancement (RIDME) [5] experiment. Unlike in PELDOR, spontaneous spin-flips are not microwave-driven, thus removing the need for a second frequency and any associated bandwidth limitations. Therefore, RIDME allows measurement of some spectroscopically orthogonal systems, such as Cu^{2+} -nitroxide for example, with greater sensitivity than PELDOR. This is particularly of interest in the context of Δ quantification; since in a spectroscopically-orthogonal system there is no decrease in modulation-depth even with a vast excess of the non-detected spin. Quantitation of modulation-depth in RIDME was recently shown [6], using standard processing methods.

In the present work, we use two quantitatively nitroxide-labelled model protein constructs, each with a distinct double-histidine Cu^{2+} -binding motif to demonstrate that modulation-depth quantitation via RIDME can be used to extract dissociation constants (K_D) throughout the μM concentration-range. Our results indicate a good agreement with expected values from fitting, and upon comparison with preliminary ITC data; suggesting this approach could be applied more generally to systems with affinities ranging from high nM to low mM K_D .

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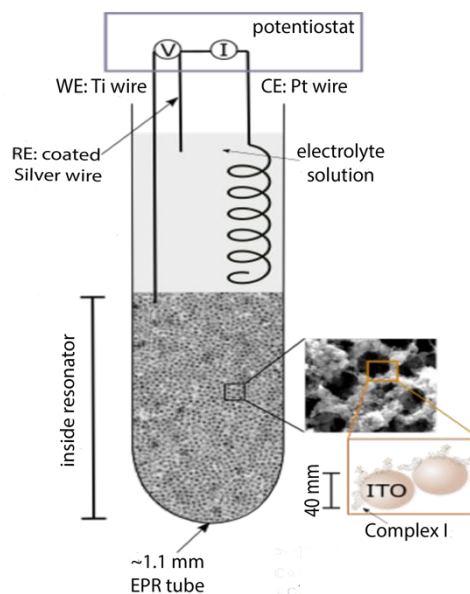
A new spectroelectrochemical technique to study (bio)catalysts

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The combination of electron paramagnetic resonance (EPR) spectroscopy with protein film electrochemistry (PFE) provides a novel platform for the investigation of reactions involving metalloenzymes such as respiratory complex I. The development of a PFE-EPR system will provide kinetic and thermodynamic information of redox reactions involving proteins during catalytic turnover with potential control. Current electrochemical-EPR setups are based on generating radical species in solution via electrolysis [1] and are limited by diffusion. Accurate potential adjustment is thus not possible with large redox active complexes, including many proteins. We aim to develop a generally applicable PFE-EPR method and use this new technique to investigate the mechanism of respiratory complex I by studying the EPR-active iron-sulfur clusters at well-defined potentials during catalytic turnover, as well as the role of quinone reduction in energy coupling.



Here, our current work towards the development of PFE-EPR is presented. We demonstrate that hierarchical indium tin oxide (ITO) structures [2] are suitable working electrode materials, offering a large surface area for protein immobilisation. The inverse-opal structure (IO-ITO) was successfully constructed inside a Q-band EPR tube (I.D. ~1.1 mm) and effective conductivity between the IO-ITO and working-electrode titanium wire was established. Sufficient sensitivity for EPR spectroscopic applications was demonstrated using a small redox-active protein, *Zea mays* Ferredoxin I (20 kDa), that was drop-cast into the IO-ITO inside the EPR tube. The resulting EPR spectrum indicates successful reduction and detection of its [2Fe-2S] cluster. Finally, efficient electron transfer between large enzymes and the working electrode relies on their orientation-selective anchoring on the surface; the IO-ITO electrode was functionalised with a Ni-NTA group and the entire respiratory complex I (*P. pastoris*, 980 kDa) was immobilised using a natural Histidine tag. Together, these results demonstrate the feasibility of a combined PFE-EPR technique.

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Conformational dynamics of mVDAC1 and the influence of tBid studied by SDSL with pulse EPR and MD simulation

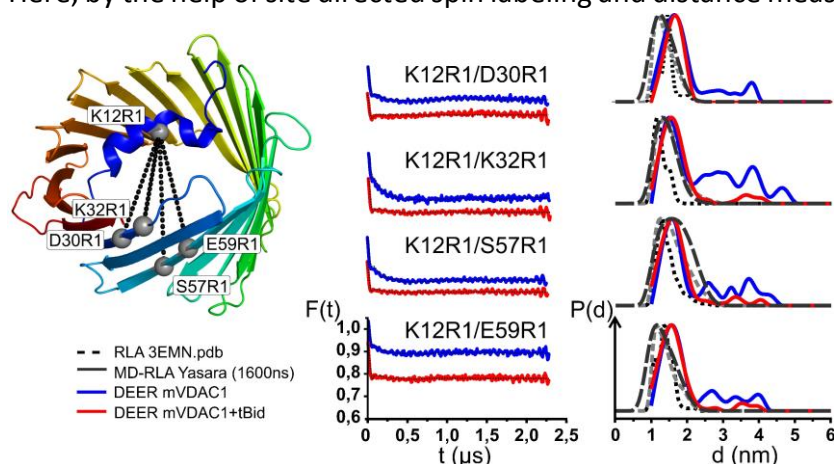
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Voltage-dependent anion channels (VDACs) are the major proteins of the mitochondrial outer membrane (MOM) of eukaryotes. They exhibit multiple physiological functions, like for instance mediating the flow of essential metabolites and ions across the MOM, regulated mainly by the membrane potential but also by the interaction with other proteins and small molecules. Furthermore VDACs turned out to play an important role in the induction of apoptosis, nevertheless, how they are involved in the apoptotic pathway is still largely unknown. [1]

The high resolution structure of murine VDAC1 revealed a 19-stranded membrane-spanning β -barrel with an α -helix located in the middle of the pore. Interestingly, this finding is contrary to the transmembrane folding patterns based on biochemical and functional studies. [2; 3] Also, how MOM permeabilization exactly occurs is still unclear or discussed contradictory. [4] Here, by the help of site directed spin labeling and distance measurements by Double electron



electron resonance (DEER) spectroscopy we studied the interaction of tBid (truncated Bid), an activated BH3-only pro-apoptotic member of the Bcl-2 protein family, on mVDAC1. We observed an influence on the inter spin distances in mVDAC1 (see Figure) upon tBid binding, suggesting that binding of tBid “closes” the anion channel by fixing the N-terminal α -helix within the pore. We compared the results from pulse EPR spectroscopy with calculated distance distributions obtained from a molecular dynamics simulation of VDAC1 in a lipid bilayer.

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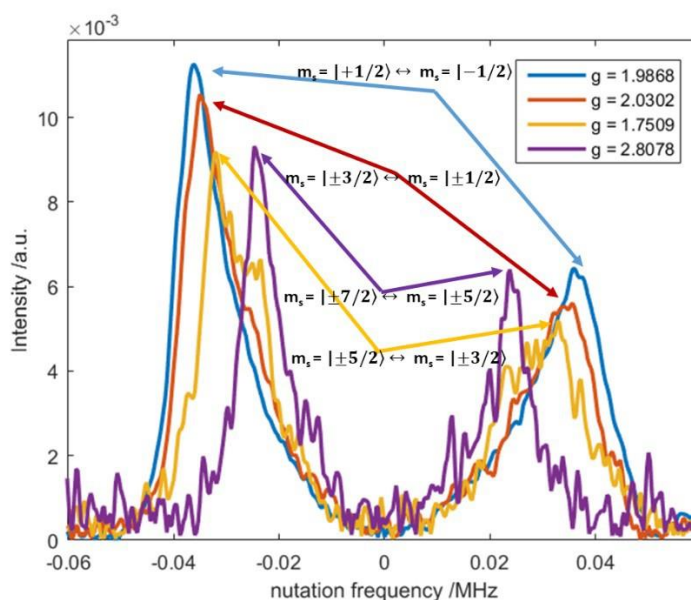


EPR of lanthanide complexes: exploring the consequences of ligand induced anisotropy

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Ligand field anisotropy plays a key role in defining the spectroscopic properties of lanthanide complexes. We have recently shown how changes to the local ligand field can have profound consequences for the NMR, luminescence and EPR properties of lanthanide ions with inherent anisotropy, such as europium and ytterbium [1]. In this study, we extend our existing work to the behavior of gadolinium complexes, where the ground state of the free ion has an isotropic electron distribution. In these systems, changes to the ligand field and the axial donor are shown to have dramatic effects on the form of the EPR spectrum. These can be rationalized through considering the donor set. A number of EPR techniques have been used to characterize the systems: CW EPR and pulsed PEANUT (phase-inverted echo-amplitude detected nutation) measurements can be correlated with the splitting of the m_s states within the 8S ground state of Gd(III). These variations, with relatively small changes to the local field, can provide useful information and aid in the development of new contrast media. The figure shows the 4 nutation frequency transitions observed in PEANUT measurements on Gd.DOTAMPh in the presence of benzylamine as an axial ligand.



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Resolving the true distance distribution in homo-multimers

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Pulse dipolar electron paramagnetic resonance (PD-EPR) has become an important tool for structural biology. Most commonly, the pulsed electron-electron double resonance (PELDOR or DEER) technique is employed to determine distances on the nanometre scale. Of special interest for PD-EPR applications are membrane proteins which are intrinsically difficult to study with crystallography or cryo-EM in all functionally relevant conformations. These proteins often form homo-multimers, which can result in the presence of more than two spin labels per protein complex if standard labelling procedures are applied. This can, in turn, lead to distorting multi-spin effects that need to be suppressed for obtaining reliable PELDOR data [1].

We have investigated two different approaches for suppression of multi-spin effects in PELDOR applications on two bacterial mechanosensitive channels (pentameric MscL and heptameric MscS). We compared the previously reported approach for reducing the excitation probability of spins (λ) [1, 2] with a sparse labelling approach, whereby the spin-labelling efficiency f is reduced. For cytosolic mutants of both proteins the latter results in significantly smaller losses in overall sensitivity, while both approaches are able to sufficiently suppress multi-spin effects if $\lambda f < 1/(n-1)$, with n being the number of spins in the system [3].

In complex biological systems the combined presence of multiple spins and multiple distances poses a number of challenges for reliable data analysis in PD-EPR. Our data demonstrate that a combination of a post-processing approach (power-scaling) [1], sparse labelling and/or λ -reduction can help overcome detrimental multi-spin effects. However, achieving sufficient accuracy and precision for reliable data interpretation is dependent on the achievable distance resolution. An initial study on the resolution of three distances in a chemical model system demonstrates that distance resolution is not necessarily achieved just by using a dipolar evolution time of twice of the inverse dipolar constant for the longest distance (*i.e.*, having two full oscillations recorded) [4].

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New insights into the B-class dye-decolorizing peroxidases: An EPR study of the heme and the radical sites in a DyP from *K. pneumoniae*

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Dye-decolorizing peroxidases (DyPs) are heme *b*-containing proteins that occur in the genomes of several fungi and bacteria. DyPs can be divided into three distinct classes (A, B, C/D) and are hailed for their biotechnological potential, including the degradation of textile dyes and lignin. However, reported peroxidase activity with conventional substrates is often low and the reaction mechanism remains confuse [1].

Here we have studied *KpDyP*, a class B enzyme from the bacterium *Klebsiella pneumoniae*, which has been expressed recombinantly in *E. coli*. Kinetic studies showed that, upon activation of the protein with equimolar H₂O₂, an extremely stable Compound I (an oxoiron(IV) porphyrin π -cation radical) is formed. Subsequent addition of specific substrates led to the first observation of an oxoiron(IV)-type Compound II in a B-class DyP [2]. This challenged the current hypothesis on the reduction steps [3].

Electron paramagnetic resonance (EPR) is highly suited to investigate the different intermediates during enzyme turnover. The resting state protein features distinct high-spin ($S = 5/2$) Fe(III) signals with varying rhombicity upon site-directed mutation of the catalytically important residues Arg232 and Asp143. Surprisingly, an organic radical is also observed in the resting state of the wild-type enzyme. Multi-frequency CW and pulsed EPR reveals the presence of at least one tyrosyl radical. An amino acid radical has, to our knowledge, never been reported in the resting state of DyPs.

Addition of a stoichiometric excess of H₂O₂ provides a Compound I spectrum similar to what was observed for HRP, demonstrating the presence of a porphyrin π -cation radical [4].

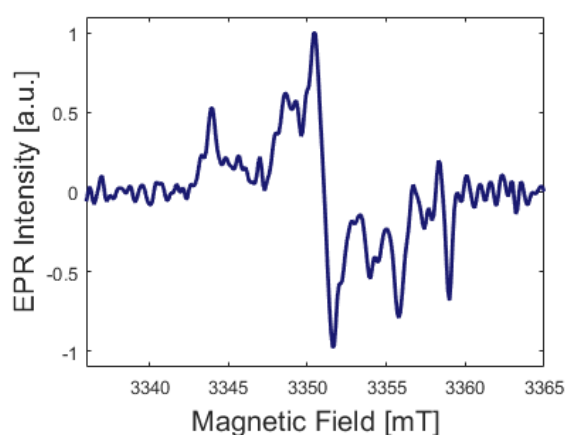


Fig. 4: W-band 1st derivative ESE-detected EPR of ferric wt *KpDyP* at 80 K.

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Integration of DEER data in Maximum Occurrence analysis

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Calculating the expected experimental observables (e.g.: NMR, EPR, SAXS,...) from a given conformation, or ensemble thereof, is an affordable task. On the contrary finding the relative population of different conformers that compose the natural ensemble from the averaged experimental observables is an ill-posed and ill-conditioned inverse problem that admits an infinite number of solutions. Several approaches have been provided over the years to address this problem [1,2]. Among those, we have proposed the Maximum Occurrence approach [3]. Maximum Occurrence is defined as the largest amount of time that the system can spend in a given conformation and still be compatible with the experimental observables. We here demonstrate how the inclusion of DEER data [4] can assist in constraining the maximum occurrence and identify those conformations that can be sampled longer consistently with the experimental data.

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Processing methods for spectra and two-dimensional distance correlation maps from pulsed triple electron resonance (TRIER)

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The recently introduced pulsed triple electron resonance (TRIER) experiment [1] allows for correlation of dipolar frequencies originating from the same molecule, which can solve the assignment problem encountered in DEER measurements when a molecule exists in several distinct conformations. In our first publication [1], spectral resolution and dynamic range in distance domain appeared to be insufficient for application to systems of biological interest. To solve this problem, we have developed new data processing methods.

Spectral resolution and artefact rejection have been improved by means of symmetrization of the spectrum about its diagonal. However, unsatisfactory background correction can still lead to spectral artifacts. We have developed a method based on the non-averaged covariance matrix of the spectrum, which serves as a matched filter and recovers the correlation peaks in the spectrum.

On top of that, we have developed new methods to obtain two-dimensional distance correlation maps from TRIER data sets. First, we implemented a two-dimensional approximate Pake transformation (2D-APT). Second, we have found that the Tikhonov approach fails as a regularization method for two-dimensional data sets. Instead, we implemented a gradient projection (GP) algorithm, which exploits the regularization properties of iterative methods, as well as an additional regularization method based on the uniform penalty principle (UPEN) [2]. These new methods perform significantly better than the Tikhonov approach and generate correct two-dimensional distance correlation maps.

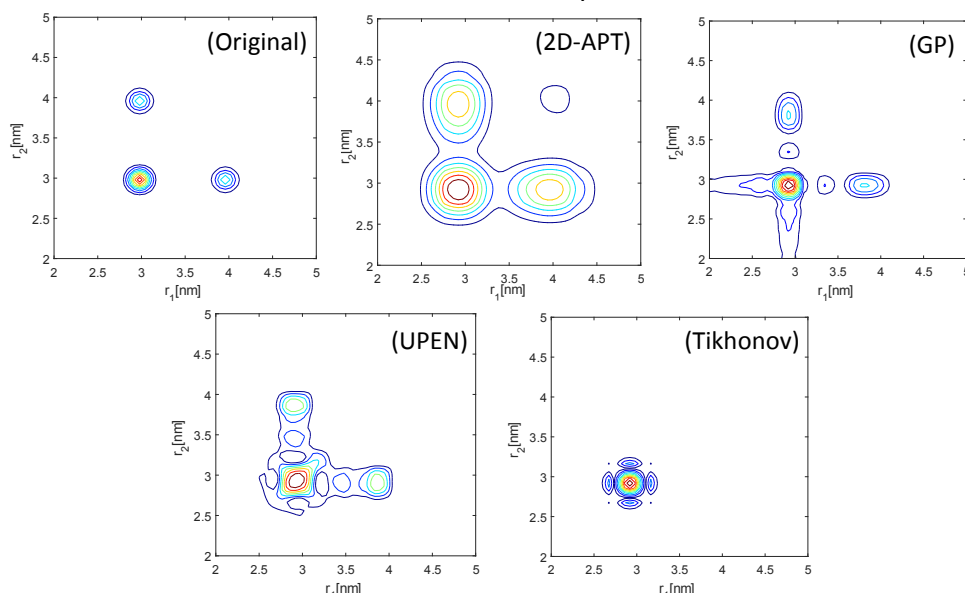


Fig. 1: Two-dimensional distance correlation maps for a simulated test signal obtained with the new methods.

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Pulsed EPR studies of an amide-based Sc(II) complex

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Many molecular systems have been demonstrated to show quantum coherence, a property that makes them suitable as quantum bits (or qubits) [1-4]. The qubits are the building blocks of a quantum computer, which will be able to carry out calculations that are never possible with a conventional computer. One key property of the qubit is its lifetime scale, measured through the phase coherence time (T_2) [1]. In the last decade, numerous groups focused their research towards designing molecules that exhibit long coherence time, one of the most stated strategy being the use of nuclear spin-free ligands [3, 4]. Another crucial property of the qubit is its ability to access any arbitrary superposition of its constituent state (i.e. observation of Rabi modulation).

Here we present pulsed EPR studies for the organometallic scandium (II) complex, a $\{\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3\}\{\text{K}(2.2.2\text{-cryptand})\}$ (**1**) [5]. Various pulsed EPR techniques, such as ESSEM, ENDOR and HSCORE, have been involved to characterize the spin state of this compound, and to study the hyperfine interactions and coherence properties. Despite the very rich nuclear spin environment (^1H , ^{14}N , ^{29}Si), the compound displays long lived quantum coherence, as well as nuclear Rabi modulations, at relatively high temperatures, probing the potential of the compound as a molecular spin qubit. We show that all electronuclear transitions in **1** are accessible for quantum information processing.

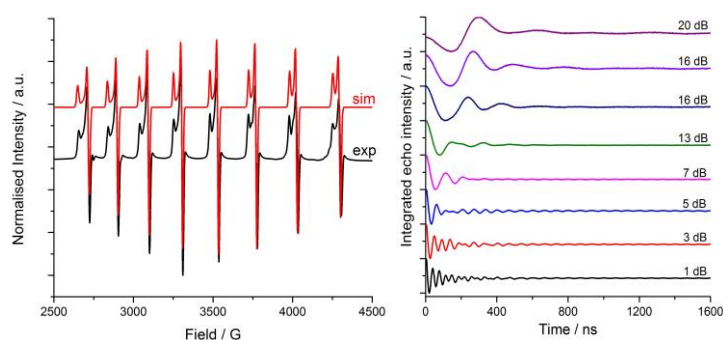


Figure 5. (left) Continuous-wave EPR spectrum and (right) Rabi oscillations at 24 K and for **1**.

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Conformational changes of Channelrhodopsin-2 investigated by time-resolved EPR spectroscopy

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Channelrhodopsin-2 is a cation-selective light-gated channel¹, which is observed as a dimer. Its manifold usage has established channelrhodopsin-2 as the most prominent optogenetic tool². Photoisomerization of the retinal leads to conformational changes of the protein, which open the channel. In contrast to other rhodopsins an outward movement of helix B during the functional process of the protein could be observed by distance measurements using pulse-EPR spectroscopy³.

The photocycle, which describes the transitions between different intermediates of the protein upon light activation, is characterized by several time constants measured by time-resolved FTIR- and optical spectroscopy^{3,4}. Mutants, which were available for distance measurements, were used here for time-resolved EPR spectroscopy to provide information about the relation between transitions of the photocycle, the helix movements, and channel formation.

The light-minus-dark difference continuous wave EPR spectrum with spin labels on helix B and helix F and the time constant for the light induced conformational change could be resolved. Furthermore, the origin of the difference spectra could be explained, utilizing EPR spectra simulations, by a transient increase of the mobility of the spin label. These results relate the observed light induced transient movement of helix B, its coupling to channel opening and closing³, to transitions between photocycle intermediates.

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Pulse EPR and ENDOR study of manganese doped $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}(\text{HCOO})_3]$ hybrid perovskite

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We use pulse EPR and ENDOR spectroscopy to investigate the manganese doped $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}(\text{HCOO})_3]$ hybrid framework based on the perovskite architecture (see Fig. 1) [1]. This compound exhibits a structural phase transition at 163 K to a ferroelectric ordered phase. The echo-detected field sweep Mn^{2+} spectrum of the disordered phase reveals a significant EPR transition-dependent relaxation. The ^1H ENDOR pattern indicates several protons in the vicinity of the Mn^{2+} center in agreement with the density functional theory calculations. A multifrequency (X, Q and W-band) electron spin echo envelope modulation (ESEEM) technique reveals a peculiar signal which is unaffected by the external magnetic field. The temperature dependence of the longitudinal relaxation time indicates a coupling between the Mn^{2+} electron spins and a hard optical phonon mode, which undergoes a damping at the phase transition point. The temperature dependent measurements of the phase memory time reveal methyl group motion in the ordered phase.

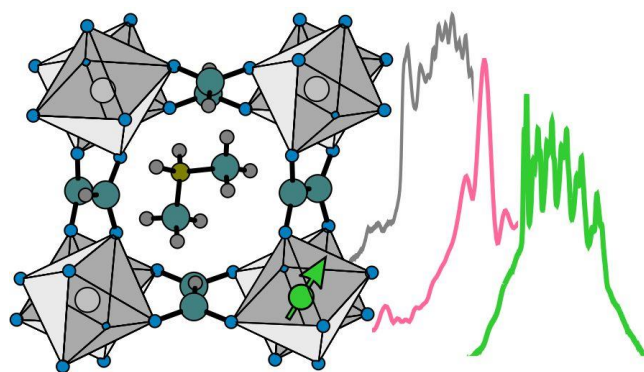


Fig. 1. Structure of $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}(\text{HCOO})_3]$ hybrid perovskite in the ordered phase (left). ^1H ENDOR, ESEEM and EDFS spectra of the Mn^{2+} centers in this compound (right).

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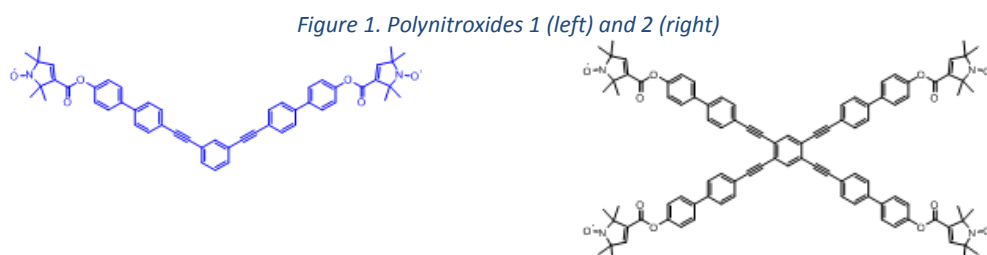


Identifying Intra-Monomer Distances by using PELDOR

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The main purpose of biophysical research is to gain insight into the mechanism of function of biomolecules. Monitoring their distances by using Pulse Electron-Electron Double Resonance (PELDOR) can help understand topologies and conformational changes during function [1]. In homo-multimers, commonly the distances between paramagnetic probes covalently bound to a specific site of each unit (protomers) are measured [1]. However, distances within one monomer are potentially more sensitive for characterising conformational changes [2]. Yet, doubly labelling monomers leads to double the number of spin labels and this reduces the reliability of the distance distributions due to multi-spin problems [3^{a-c}]. In this contribution, mixtures of different ratios of two polynitroxides consisting of spin labels attached to the end of rigid spacers [4] (Figure 1) are used as a model. Compound **2** resembles a dimer of compound **1**. Different experimental and data analysis approaches were tested in conjunction with numerical simulations with the aim to establish the minimum **1:2** ratio that allows the unique identification of an intra-monomer distance. Ultimately, we aim to test the feasibility of the intra-monomer distance identification on proteins and in this poster, the first results on a dimeric protein model will be presented.



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Electronic structure of three isostructural nine-coordinate lanthanide families with small crystal field splitting: a combined experimental and *ab initio* study

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We recently reported the theoretical and experimental study of NMR and luminescence properties in solution of the nine-coordinated lanthanide series $[\text{LnL}^1]$ (Ln = Eu, Tb, Dy, Ho, Er, Tm, and Yb; H_3L^1 : 1,4,7-tris[(6-carboxypyridin-2-yl)methyl]-1,4,7-triazacyclononane). As a consequence of the peculiar C_3 -symmetric nine-coordinate geometry of the $[\text{LnL}^1]$ series in solution, the second rank zeroth order crystal field parameter B_2^0 has a near-zero value whose sign can be changed by minimal structural perturbations, such as those induced a change of solvent; this has dramatic consequences for the NMR pseudocontact shifts [1].

Following these results, we have turned our attention to the solid state magnetic properties of the $[\text{LnL}^1]$ series (Ln = Tb, Dy, Ho, Er, Tm, and Yb), as well as to two structurally related series $[\text{LnL}^2]$ (Ln = Tb, Dy, Ho, Er, Tm, and Yb; H_3L^2 = Phosphinic acid, P,P',P'' -[(hexahydro-1*H*-1,4,7-triazonine-1,4,7-triyl)tris(methylene-6,2-pyridinediyl)]tris(*P*-phenyl-), and $[\text{LnL}^3](\text{CF}_3\text{SO}_3)_3$ (Ln = Tb, Dy, Ho, Er, Tm, and Yb; L^3 = 2-Pyridinecarboxamide, 6,6',6''-[(hexahydro-1*H*-1,4,7-triazonine-1,4,7-triyl)tris(methylene)]tris[N-[1-phenylethyl]-] (Figure 1).

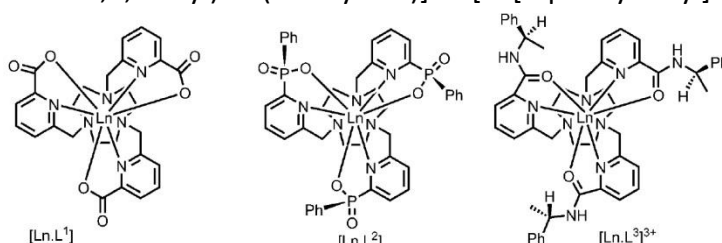


Figure 1. Schematic representation of the $[\text{LnL}^1]$, $[\text{LnL}^2]$, and $[\text{LnL}^3]^{3+}$ series of complexes.

The three series have been characterised by X-ray diffraction, SQUID magnetometry, multifrequency electron paramagnetic resonance (EPR) and *ab initio* calculations. Our results show that the magnetic data are well reproduced by *ab initio* calculations based on the solid state structure, however our EPR results cannot be reproduced without taking a distribution of B_2^0 into account. We find that the EPR signal is highly sensitive to the strain model, requiring explicit account of the distribution of spin Hamiltonian parameters, as opposed to a phenomenological strain model as is often assumed.

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Elucidation of the mechanism of the intramolecular cyclisation of allyl 2-bromobenzyl ether by *in-situ* EPR spectroelectrochemistry and DFT calculations

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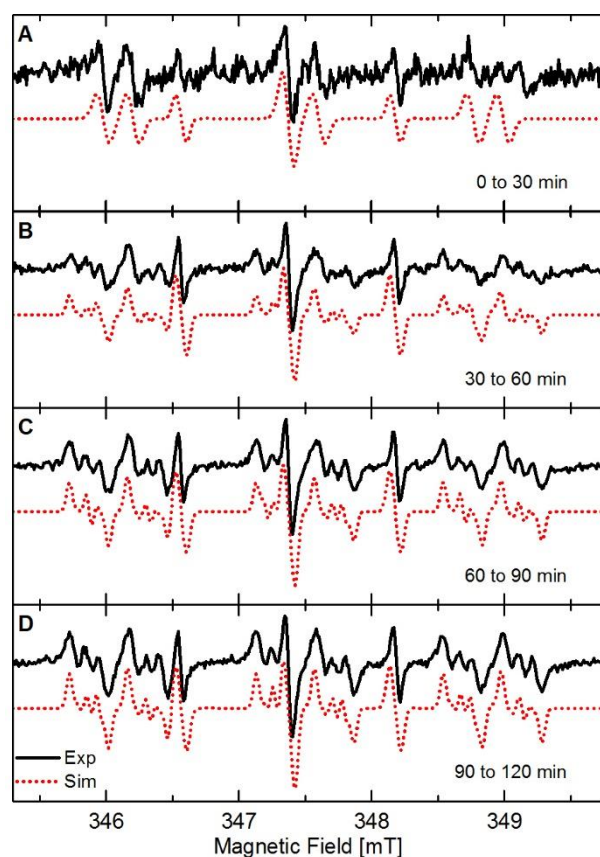


Figure 6. Accumulated experimental (black) and simulated (red) CW EPR spectra of the radicals spin-trapped during allyl 2-bromobenzyl ether cyclization reaction in different time steps

using DFT computations. A comparison of these results and their implications on the cyclisation mechanism will be discussed.

Heterocyclic compounds are vital in the pharmaceuticals, pesticides, dyes and synthetic applications. Organic electrosynthesis offers a clean, catalytic, inexpensive and environmentally friendly method for the synthesis of these compounds [1]. A profound understanding of the reaction mechanism and the influence of the electrocatalyst allows optimal tuning of the electrocatalytic process. This can be achieved by combining electrochemical techniques with electron paramagnetic resonance (EPR) spectroscopy.

In this work, EPR was used to study the electrochemical cyclisation of allyl 2-bromobenzyl ether in a home-built inexpensive electrochemical cell adapted to *in-situ* EPR. The organic radicals that were produced *in-situ* during the electrochemical process were spin-trapped by phenyl-tert-butyl-nitrone (PBN), and EPR spectra were recorded at different time steps (Figure 1). The EPR parameters of the different spin-trapped radical adducts were determined via spectral simulations using EasySpin. Possible adduct structures, possible conformations and corresponding EPR parameters were calculated

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Studying Dps–flavoprotein WrbA interaction using CW-EPR spectroscopy

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For most organisms, iron is an essential element that mainly contributes as a cofactor of many different proteins and enzymes. The bioavailability of iron at physiological conditions is poor due to its low solubility in aqueous solutions. The Fe(III) form is extremely insoluble, whereas the Fe(II) form is relatively soluble, although very toxic in the presence of O₂, potentiating the non-enzymatic production of reactive oxygen species (ROS). As such, organisms have developed mechanisms to acquire and concentrate iron and thus resist to ROS toxic effects, keeping an effective iron homeostasis. A main strategy is the production of enzymes that store iron in a non-toxic ferric form and simultaneously degrade ROS and their precursors.

Dps, DNA-binding protein from starved cells, belongs to the ferritin class of proteins is a bacterial protein involved in iron homeostasis and DNA protection. It catalyzes the fast oxidation of Fe(II) ions removing H₂O₂ from the intracellular medium. ^[1-4]

To understand the iron release mechanism from the protein inner cavity, the interaction of Dps with a putative physiologic redox partner, the flavoprotein WrbA, is being analyzed by CW-EPR spectroscopy using a nitroxide spin probe. Preliminary results seems to indicate that the N-terminus of each 12-subunits is involved in the docking between the two redox partners.

This work was also supported by Fundação para a Ciência e a Tecnologia (FCT/MEC), Radiation Biology and Biophysics Doctoral Training Programme (RaBBiT, PD-F, PD/00193/2012); UID/Multi/04378/2013 (UCIBIO); UID/FIS/00068/2013 (CEFITEC); and grant number SFRH/BD/106034/2015 to NA

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Nitrite reductase activity of GLB-33, a unique chimeric globin in *Caenorhabditis elegans* examined with EPR and UV-vis spectroscopy

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Globins are versatile proteins widespread throughout life which have many biologically relevant functions aside from oxygen binding and transport, such as the involvement in redox signaling, NO metabolism and reproduction. Out of the 34 glb genes which are all expressed in the nematode *C. elegans* [1], our interest goes to the glb-33 gene which is the largest of its kind. It is unique within the globin family because it consists of a globin domain connected to a G-protein coupled receptor domain (GPCR). Here we show the globin domain (GLB-33GD) of the full-length glb-33 gene that was expressed in the bacterium *E. coli*, purified and examined using optical (UV-vis absorption spectroscopy), CW and pulsed EPR methods. Spectrophotometric analysis of GLB-33GD shows a tenfold higher nitrite reductase activity compared with other globins [2]. This may be due to the highly hydrophobic environment of the heme pocket, the high reducing potential of the heme or the easy accessibility of the heme iron by the NO₂⁻ anion. Especially the Arg E10 residue is thought to play a stabilizing role in OH ligation, but its role in NO₂⁻ stabilization has yet to be resolved. An integrative toolbox of optical and EPR methods is necessary to fully characterize the heme pocket of this interesting globin [3]. In a first approach, the nitrite and NO ligation will be discussed and site-directed mutagenesis of heme-surrounding amino acids allows to dissect the molecular mechanism behind the fast nitrite reductase activity.

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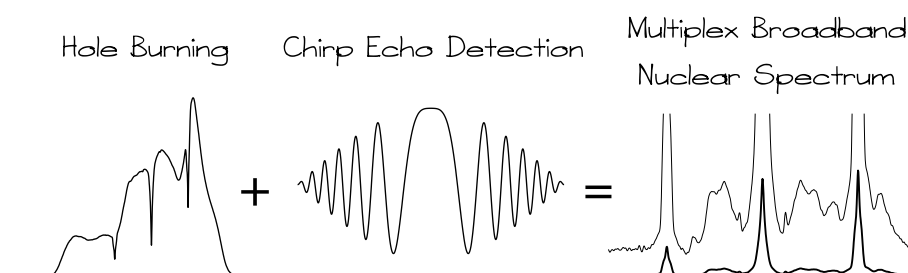


Chirp echo FT EPR-detected NMR

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Nuclear frequencies in general and hyperfine couplings in particular can give valuable information about the local structure of paramagnetic centers. One way to measure these frequencies by pulse EPR is electron-electron double resonance-detected NMR (ELDOR-detected NMR, EDNMR) [1]. This approach uses high turning angle (HTA) pulses to drive forbidden transitions. Such an HTA pulse partially saturates the allowed transitions which share a common level with the driven forbidden transition and thus creates side holes. The positions of these side holes with respect to the frequency of the HTA pulse encode the nuclear frequencies. EDNMR uses a spin echo- or FID-integral detection with fixed frequency and an HTA pulse with stepwise varied frequency. We introduce an alternative method based on chirp echo EPR spectroscopy (CHEESY) [2]. The complete hole pattern generated by an HTA pulse can be acquired in a single shot by a chirp echo detection and subsequent Fourier transform. This is a revival of FT EPR-detected NMR [3], but is also applicable to disordered systems with broad side holes and large couplings. Experimental results obtained in Q band are presented for nitroxide radicals and hexaquaamanganese(II). For the latter sample, holes over a range of >600 MHz can be detected.



The multiplex advantage of the CHEESY-detected NMR approach facilitates the introduction of additional dimensions. The hyperfine spectrum can be correlated to the EPR spectrum by changing the frequency of the HTA pulse and leaving constant the magnetic field and detection sequence. Different side holes can be correlated to each other by applying a π pulse at the position of a side hole before the HTA pulse. This π pulse saturates the connected forbidden transition, and a subsequent HTA pulse does not have an effect any more. The obtained information is similar to HYSORE, i.e. peaks are identified that belong to the same nucleus and the coupling regime is unraveled. This approach complements the recently introduced 2D-EDNMR [4], which employs two HTA pulses to correlate frequencies of different nuclei, and it could also be used without the chirp echo detection.

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EPR spectroscopy and in situ EPR/UV-vis-NIR spectroelectrochemistry of nickel based macrocyclic complexes as potential catalysts for production of energetically rich materials

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In the presented contribution the redox behavior of newly prepared macrocyclic nickel complexes is studied by cyclic voltammetry, EPR and in situ EPR–UV/vis/NIR spectroelectrochemistry. Special attention is focused on the characterization of the redox site for both oxidation and reduction, in different organic solvents and at various experimental conditions (CO₂ or H⁺ presence, different temperatures, various working electrodes). Quantum-chemical calculations of investigated complexes at the B3LYP/6-311g* level of theory in different charge and spin states allow us to interpret the experimental EPR and spectroelectrochemical results. Generally the reduction potential and reversibility strongly depend on the number of phenyl or methyl substituents on the macrocycle ring indicating a ligand based reduction. In contrast to the cathodic reduction, the anodic oxidation is considerably less sensitive to changes in macrocycle substitution pattern, suggesting a partial contribution of the central Ni(II) atom to the redox behavior. The reversibility and redox mechanism in the region of the first reduction peak for Ni(II)L macrocyclic complexes was further investigated by the in situ spectroelectrochemical UV-vis-NIR cyclic voltammetric experiments in a special thin layer honeycomb spectroelectrochemical cell [1]. A broad slightly anisotropic EPR spectrum with g-value $g_{iso} = 2.0004$ characteristic for ligand based radical was observed confirming a purely ligand based reduction. On the contrary, the rhombic EPR signal with a rather large g-tensor anisotropy, obtained at low temperatures (100 K) upon one-electron oxidation, indicates the formation of a ligand-centered radical with pronounced delocalization of the unpaired spin into the orbitals of nickel ion [2].

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Electronic Communication in Bis-Copper Porphyrin Oligomers

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A detailed understanding of the structural requirements for an efficient electronic communication between two spin centres is at the basis of the further development and improvement of applications in the field of molecular electronics. In the present work, we use continuous wave and pulse EPR spectroscopy to investigate intramolecular electronic communication in different series of bis-copper porphyrin oligomers. The investigated structures differ in (i) their structural rigidity, (ii) the inter-spin distance and relative orientation of the spin centres and (iii) the nature of the bridge between the porphyrin units.

We demonstrate that molecular templates can be used to conveniently control the geometry and rigidity of the structures [1]. Depending on the strengths of the intramolecular interactions, different simulation approaches will be presented to separate the contributions of through-space (D) and through-bond (J) couplings and determine their individual magnitudes and distributions [2,3].

The systematic comparison of the obtained results will be shown to yield valuable information on the influence of the molecular geometry on coupling efficiency and may help to establish structure-function relationships for efficient long-range electronic communication.

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Spin dynamics of potential molecular qubits in thin films

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Spin dynamics play an important role for a potential application of paramagnetic transition metal complexes as qubits. The quantum coherence time of a qubit, which is related to how long the qubit can preserve its superposition, is directly related to the phase memory time T_m of a molecular qubit. In the case of diluted paramagnetic transition metal complexes, the limiting factor of T_m is often nuclear spin diffusion caused by protons. It is well known, that deuteration of the surrounding of the spin center increases T_m by approximately one order of magnitude. However, no quantum mechanical qualitative calculations of T_m were carried out on this kind of systems, as one would have to consider a huge bath of nuclei making the calculations very demanding. Fortunately, we were able to adopt a literature known method treating nuclear spin diffusion in the P@Si system to our molecular systems. This method preserves the quantum mechanical nature of nuclear spin diffusion without assuming a statistical model for fluctuating fields. We used this method to simulate the primary echo decay of $\text{Cu}(\text{dbm})_2$ in $\text{Pd}(\text{dbm})_2$ using the positions of the protons (and thus the dipolar couplings) obtained from the crystal structure of $\text{Pd}(\text{dbm})_2$ alone. The simulation fits perfectly in this case, as well as for $\text{Cu}(\text{mnt})_2^{2-}$ in $\text{Ni}(\text{mnt})_2^{2-}$ and other systems where nuclear spin diffusion is the main source of decoherence.

We believe that for real world applications, thin films of molecular qubits will play an important role in order to interface the qubits with our current semiconductor technology. Therefore, we started to investigate thin films of paramagnetic molecules to get a better understanding of spin dynamics in thin films. As a first step, we developed a Fabry-Pérot resonator allowing us to measure large substrates covered with nanometer thin films. Our first results on 40 nm – 600 nm films of BDPA diluted in a polystyrene on silicon show that the spin-lattice relaxation time is strongly dependent on the film thickness.

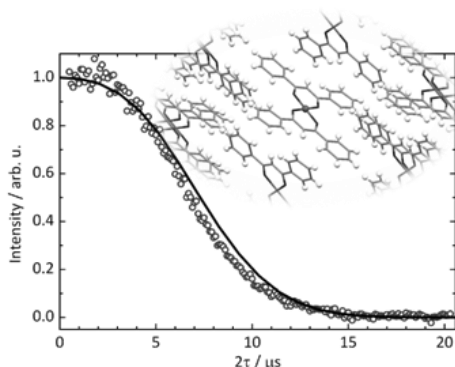


Figure 7 Hahn-Echo decay of $\text{Cu}(\text{dbm})_2$ in $\text{Pd}(\text{dbm})_2$ (dots). The decay was simulated (black line) using a quantum mechanical model which accounts for nuclear spin diffusion.

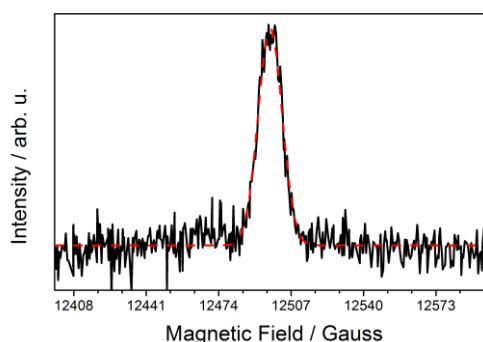


Figure 2 Echo-detected EPR spectrum of a 40 nm film of BDPA diluted in polystyrene at 7 K and 35 GHz

[1] S. Lenz, K. Bader, H. Bamberger, J. van Slageren *Chem. Commun.*, **2017**, 53, 4477-4480





DEERNet – a deep neural network for DEER data processing

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It is demonstrated that deep neural networks (DNNs) are a powerful alternative to Tikhonov regularisation methods for the interpretation of DEER data. Networks trained using large databases of synthetic DEER traces with carefully modelled distortions and noise are found to process previously unseen experimental data with results comparable to, and occasionally better than, the state-of-the-art Tikhonov methods.

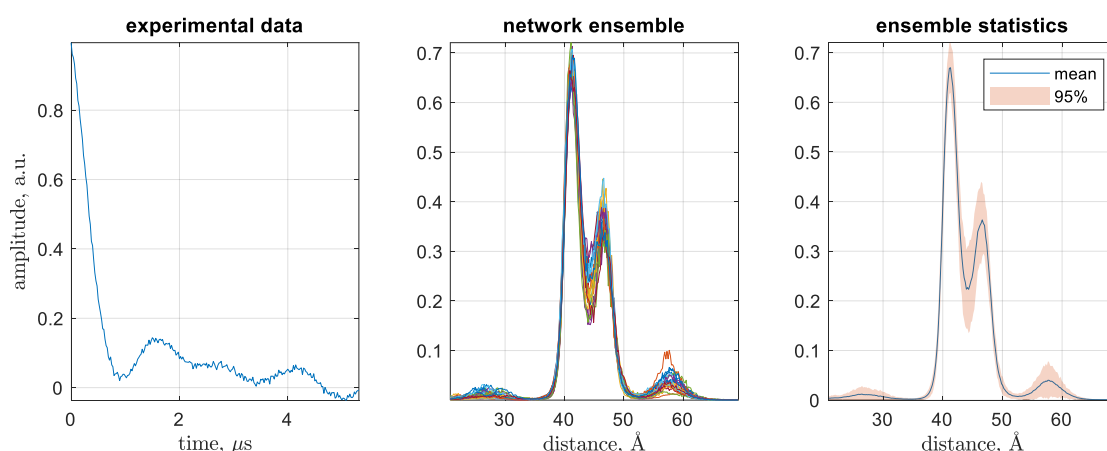


Figure 8. DEERNet output for the I143C, V96C mutant in the luminal loop of plant light harvesting complex LHCII. A bimodal distribution is seen, in agreement with expectations and with Tikhonov reconstruction [3]. The neural network is a single Matlab function with no adjustable parameters.

The current best practice for DEER processing is to use Tikhonov regularised deconvolution, a procedure that works well in simple spin- $\frac{1}{2}$ pairs, but becomes difficult for more complex systems [1]. Using DNNs trained on simulated data is attractive because future training data can be generated to include all complications. Such neural networks would be resilient to the presence of zero-field splittings, exchange, and out-of-pair inter-electron interactions.

DNNs performance strongly depends on the quality of the training dataset. To ensure that the network can successfully process previously unseen datasets, the training database must be representative of the entire range of real experimental systems. The relevant functionality has recently become available in the *Spinach* library. There are also important factors around the network architecture, pre- and post-processing of data, and the training process [2].

In this communication we introduce *DEERNet* and describe how we have created the training database, tuned the network parameters, and handled data pre-processing to achieve excellent performance on real-life DEER data.

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Orthogonal labelling strategies to study protein interaction networks

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The BIM BH3 peptides have potential as pro-apoptotic protein-mimicking drugs that can kick-start apoptosis in uncontrollably replicating cancer cells [1]. In fact, they perturb the Bcl-2 protein network [2] by synergistically activating proapoptotic proteins (such as Bax) and inhibiting antiapoptotic proteins (such as Bcl-XL). We have produced single and double cysteine mutants of a 26 and a 16 amino acid version of BIM peptide, and labelled it with multiple-purpose nitroxide, copper and gadolinium spin labels by adding cysteine residues at the N and C termini. We characterized the peptides by CW EPR and DEER spectroscopy complemented by CD and NMR spectroscopy.

To verify that differently labeled peptide variants retain their activity we used a combination of EPR kinetics and vesicle permeabilization assay experiments in the presence of Bax, Bcl-XL and membranes, which offers a basis for strong conclusions of the structure-function relationships of BIM BH3 peptides and the Bcl-2 protein partners. Additionally, we labeled Bcl-XL at its natural cysteine to directly measure the binding of the peptides and follow their effect on the intrinsic oligomerization of the Bcl-XL proteins, exploiting the use of spectroscopically orthogonal pairs. The fingerprint distances of the protein interaction network in vitro will simplify the analysis of measurements using reduction-resistant nitroxide spin labels or functionalized Gd^{III} or Cu^{II} chelators with freshly isolated mitochondria.

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Structural Characterisation of *Danio rerio* Cytoglobins

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Cytoglobins (Cygb) are heme proteins that are ubiquitously expressed in vertebrates. Unlike most mammals which only have one Cygb, members of the teleost family such as *Danio rerio* have two different Cygb coding genes[1]. As the functions of both proteins (*D. rerio* Cygb-1 and *D. rerio* Cygb-2) are currently unknown, we have used EPR, resonance Raman, and UV-vis spectroscopy to characterize the structure of their heme pockets as well as their activity with substrates such as CO and NO. The results of this work, which suggest an oxygen carrier function for *D. rerio* Cygb-1 and a more protective function for *D. rerio* Cygb-2, will be discussed with comparisons to related proteins such as human cytoglobin.

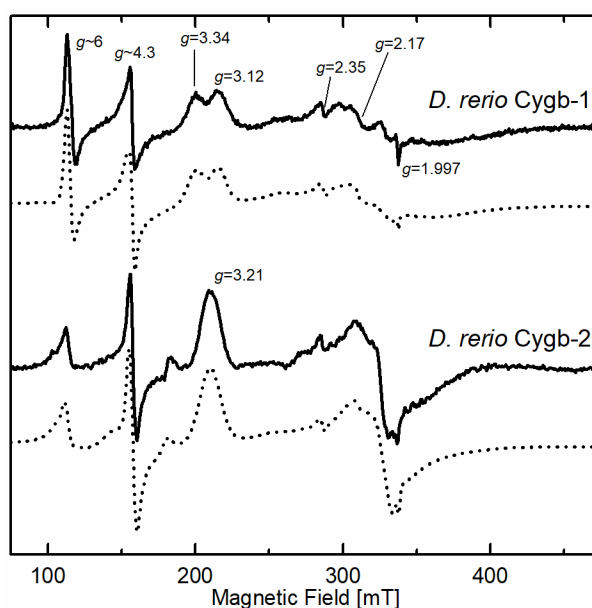


Fig. 1. X-band cw EPR spectra and simulations of *D. rerio* Cygb-1 and *D. rerio* Cygb-2 in a frozen solution recorded at 10 K.

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Investigating the role of an arginine residue near the iron-sulfur cluster N2 in complex I

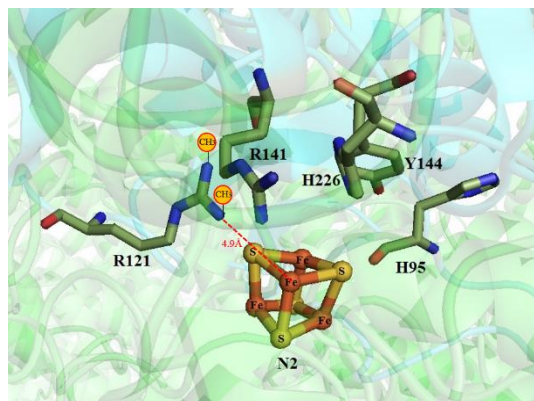
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NADH:ubiquinone oxidoreductase (complex I) is an essential component in the mitochondrial respiratory chain that contributes to the proton motive force essential for ATP synthesis. As the terminal Fe-S cluster of the electron-transfer chain that links NADH oxidation and quinone reduction and, given its close proximity to the ubiquinone binding site (Q site), N2 has long been proposed to couple electron and proton translocation [1]. Although we have recently shown that N2 is not directly involved in the coupling mechanism [2], the cluster may play an indirect role, e.g. by providing protons to ubiquinone.

Here, we investigate the function of an arginine residue (R121) from the NUCM subunit on the nearby N2 cluster in *Y. lipolytica*. We find that the R121M mutation leads to decreased complex I activity and decreased sensitivity towards the ubiquinone site-specific inhibitor piericidin A, indicating that the affinity of both substrate and inhibitor binding in the mutant is compromised. The loss of N2 EPR signals in R121M further supports the critical role of this residue for complex I function. Even the mildest mutation R121K abolishes the N2 EPR signal. Another interesting feature of this residue is that R121 is symmetrically dimethylated at its



guanidine group in *Y. lipolytica*, *B. taurus*, *H. sapiens* but not in *E. coli* complex I. Notably, the reduction potential of N2 cluster in *E. coli* complex I is relatively lower than that in other species. We have identified the gene encoding the arginine methyltransferase in *Y. lipolytica* which is responsible for this modification. This gene will be knocked out in order to investigate the possible effect of this dimethylation on the reduction potential of N2 and the proton-pumping ability of the enzyme.

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Reversible H₂ coordination to a Fe(I) complex, monitored by ESR in solution and in the solid state

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Although several small mono-metallic molecular catalysts have recently been reported by the groups of J. Peters and Nishibayashi as potential replacements to the energetically-expensive Haber-Bosch process for conversion of N₂ to NH₃, similar results are possible based on a new understanding of chemistry of the earliest and synthetically simple ligands, DEPE and DMPE [1].

To avoid issues of solvent interactions with the metal complex, CW-EPR is used to detect gas exchange in solid films, wherein a dramatic shift in g-matrix values occurs and this is attributed to ligand rearrangement in the solid state. The characterization of the H₂ is performed with ¹H- and ²H-HYSCORE and ¹H-ENDOR, consistent with literature [2]. The bisphosphine ligand platform binding to a dinitrogen adduct in the previous studies are compared by temperature dependence indicating the thermodynamic stability of dinitrogen and dihydrogen complexes. Catalytic reaction mixtures that form hydrazine, are shown to contain the N₂-coordinated species as an intermediate [3].

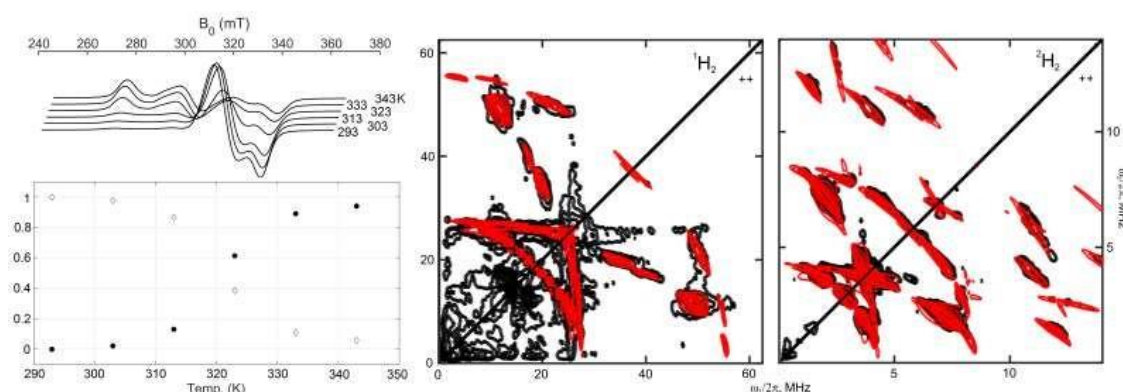


Figure 1. CW-EPR of a solid film under 1 eq. of H₂ gas (left), and ^{1,2}H-HYSCORE of frozen solution, g=2.023.

Support: Royal Society for a University Research Fellowship (A. Ashley), W.K.M. is supported by the UK EPSRC (EP/L011972/1, grant to CAESR).

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Spectroscopic analysis of myoglobin and neuroglobin immobilized on mesoporous materials

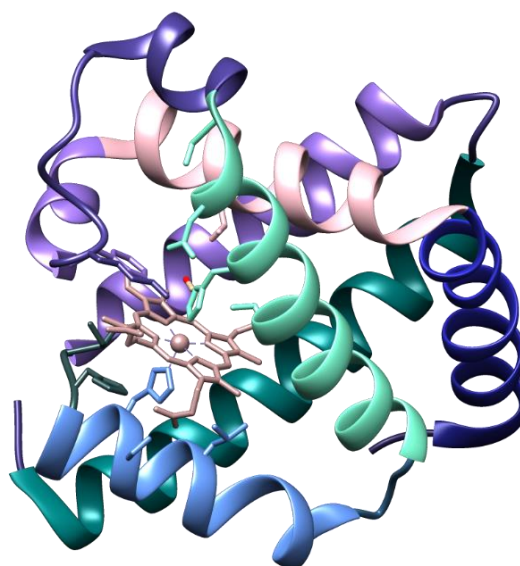
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The incorporation of globins in mesoporous materials is an important and promising direction for biosensing and biocatalysis. The immobilization cannot only stabilize the heme proteins but also improve the activity in the appropriate environment. In particular, the properties of these immobilization matrices should avoid loss of the protein activity and leaching or degeneration of the proteins. The electrochemical activity is enclosed in the heme group of the globin, where the change of the oxidation state of the heme iron can be detected in biosensing applications. These type of biosensors can be used for the detection of small molecules like H₂O₂, H₂S and NO₂⁻. Two different globins will be incorporated, namely horse heart myoglobin (hhMb) and human neuroglobin (NGB). Mb, one of the best-known proteins, is an oxygen-storage protein found in muscle cells with dimensions about 45 x 35 x 25 Å. In contrast, the function of NGB is still uncertain. NGB is predominantly expressed in the nervous system and the structure of NGB displays the typical globin fold as Mb. NGB is extremely stable under pH and temperature conditions known to denature other globins and, under in vitro conditions, it is redox active. For the encapsulation of Mb and NGB, SBA-15-type silica and titanium dioxide are used. These mesoporous materials show high biocompatibility and good retention of the protein activity. Besides the large surface area and pore volume, the size and the morphology of the mesopores are easily fine-tuned. Electron paramagnetic resonance (EPR) allows to study the ferric heme center and thus check the stability and state of the globin and its heme group before and after immobilization. Surprising differences in the behavior of the two proteins upon incorporation become apparent via this technique.



TiO₂/Bi₂O₃ heterojunction photocatalysts – visible light activity

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Among various strategies to increase the concentration of charge carriers and to suppress electron-hole recombination in semiconductor (SC) photocatalysts, the construction of suitable heterojunctions provides effective improvement of charge transfer characteristics [1]. In addition to the enhanced separation of photogenerated electron-hole pairs, which potentially leads to an overall photocatalytic efficiency increase, creating a SC/SC heterojunction with a visible-light-responsive semiconductor (e.g. β -Bi₂O₃ [2]) extends the photocatalyst application towards visible region.

A series of TiO₂/Bi₂O₃ composites was prepared with TiO₂ of different morphology (nanorods or nanoparticles) and varying amounts of a narrow band gap semiconductor β -Bi₂O₃ (**B**), e.g. TiO₂ nanorods (**T**) were combined with **B** to form a TiO₂/Bi₂O₃ junction in **TB** composite. Solid state Q-band EPR spectra obtained at 100 K under dark refer to the paramagnetic centers typical for the oxygen depleted TiO₂ present in the material prior to photoexcitation. Character of these signals reflects TiO₂ phase composition and structure, and changes in the spectra upon increasing loading of Bi₂O₃ in the composite are observed.

The formation of reactive oxygen species (ROS) upon UV ($\lambda_{\text{max}} = 365$ nm) or visible-light photoexcitation of the studied composite photocatalysts in water or dimethylsulfoxide suspensions was followed by EPR spin trapping technique. Application of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin trapping agent brought evidence of ROS generation upon visible-light exposure (Fig. 1). Detailed analysis of the character and amount of ROS generated by the photoexcitation of the individual photocatalysts can help to suggest plausible carrier migration cascade in the TiO₂/ β -Bi₂O₃ heterojunctions upon visible-light exposure.

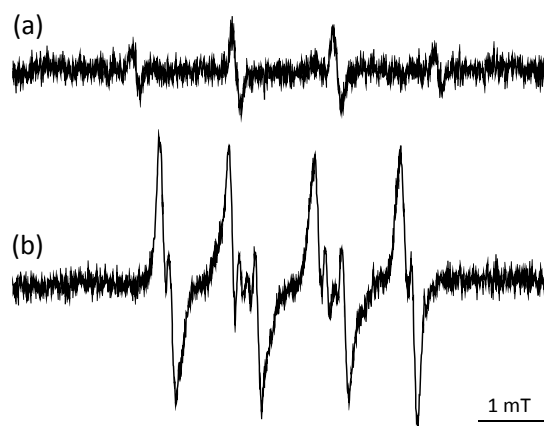


Figure 1. X-band EPR spectra obtained upon visible-light photoexcitation of **TB** dispersed in (a) water or (b) dimethylsulfoxide in the presence of DMPO spin trapping agent under air.

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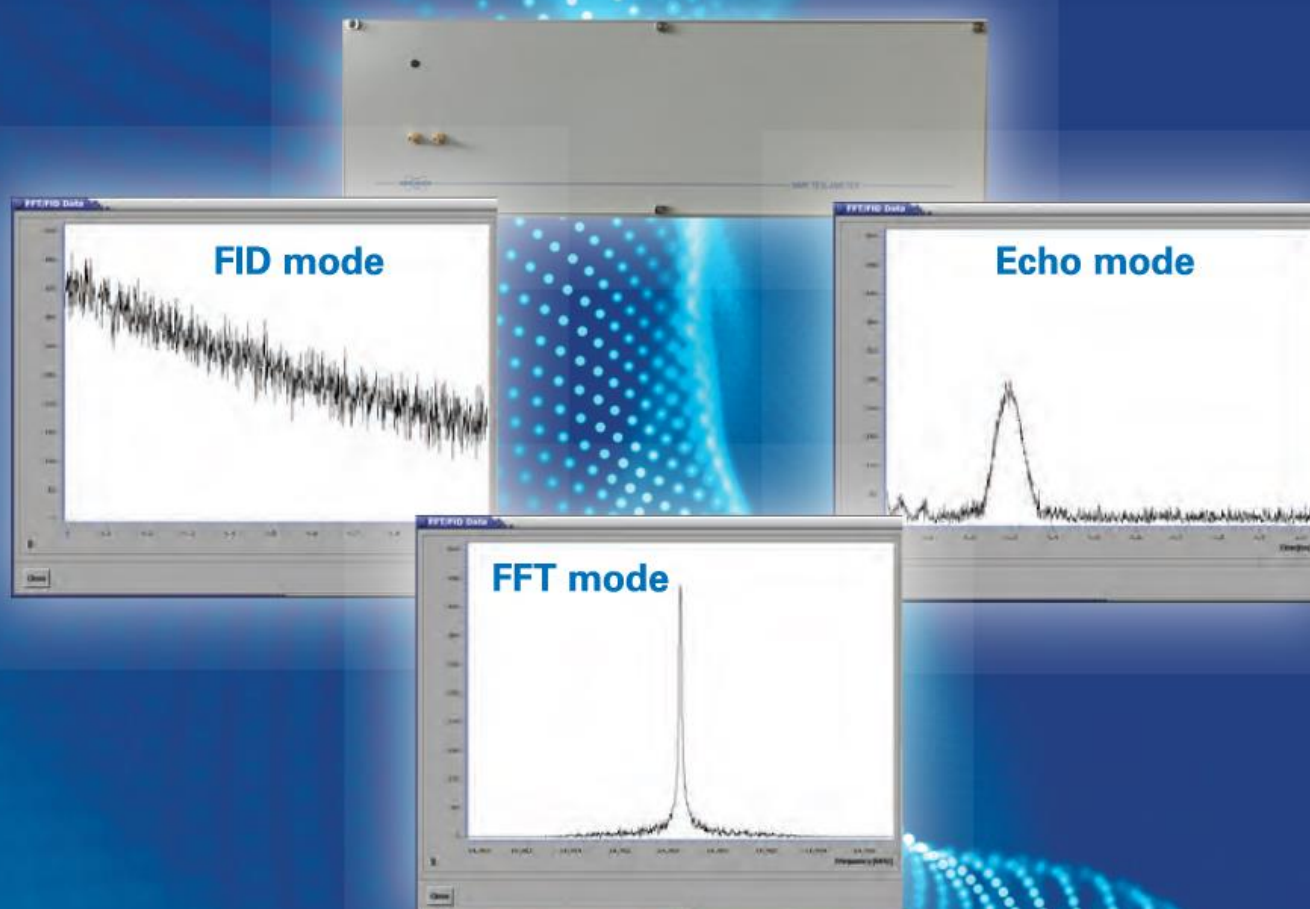


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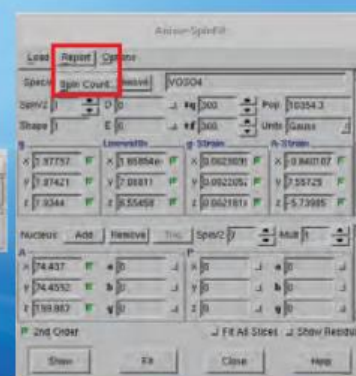
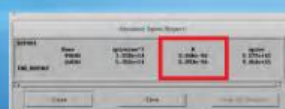
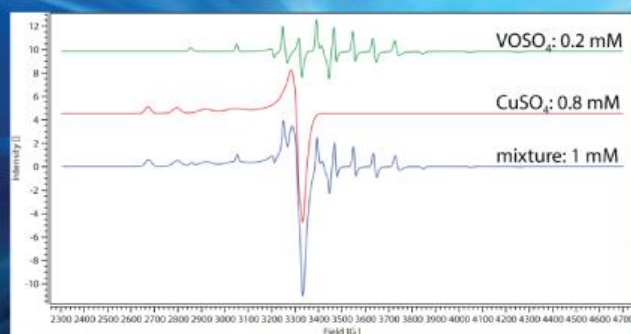
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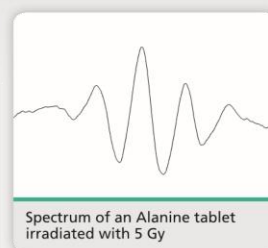
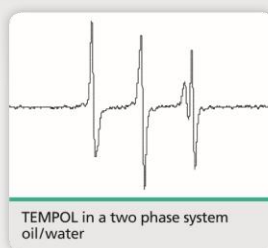
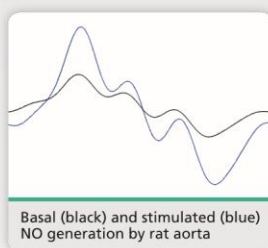
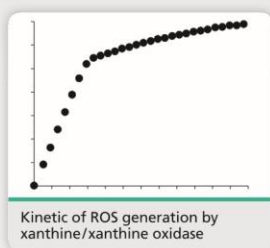


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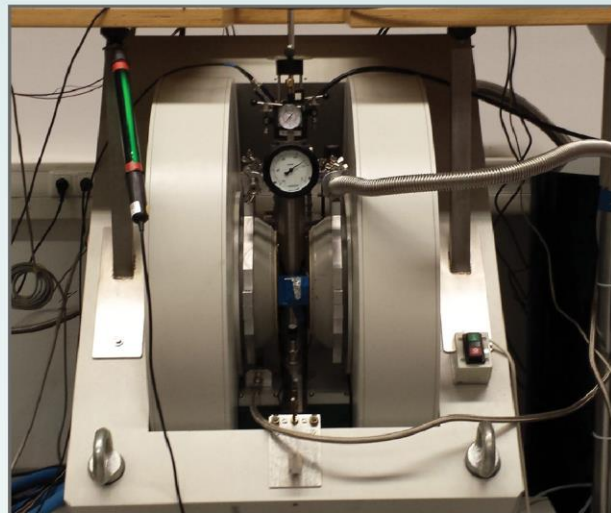
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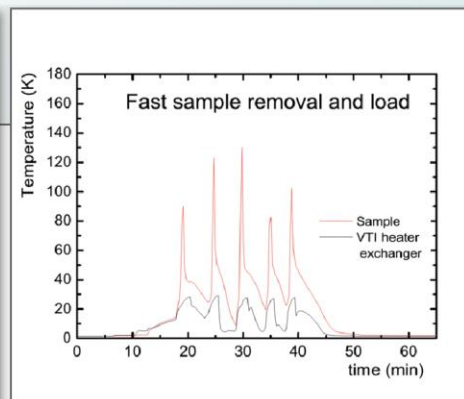
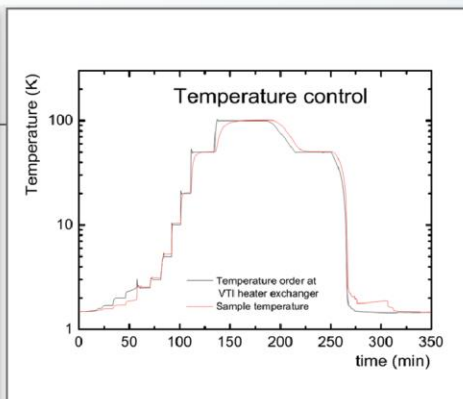
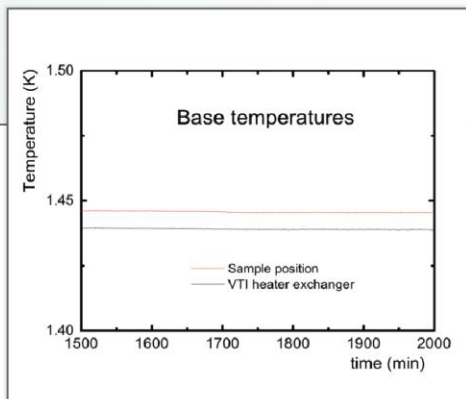
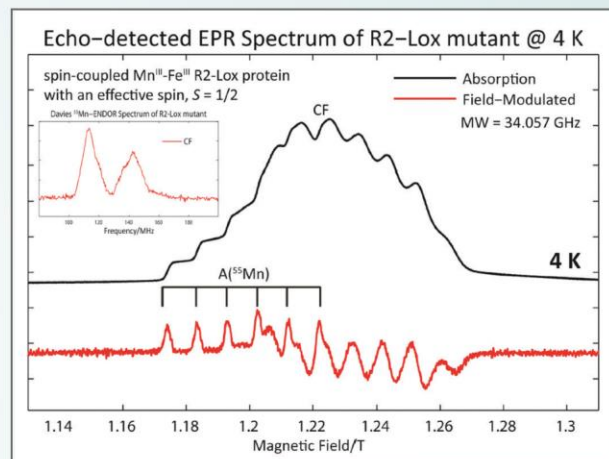


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