



THE 52<sup>nd</sup> ANNUAL INTERNATIONAL MEETING  
*of the*  
ESR SPECTROSCOPY GROUP  
*of the*  
ROYAL SOCIETY OF CHEMISTRY

UNIVERSITY OF GLASGOW  
7 – 11 APRIL 2019

On behalf of the ESR Spectroscopy Group of the Royal Society of Chemistry, welcome to the 52<sup>nd</sup> Annual International Meeting of the Group held at the Golden Jubilee Conference Hotel in Clydebank, Glasgow. The scientific sessions are headlined by our plenary and keynote speakers, as well as the recipient of the 34<sup>th</sup> Bruker Prize, Marina Bennati, and 5<sup>th</sup> Bruker Thesis Prize, Claire Motion. For younger researchers, the 22<sup>nd</sup> Annual JEOL Prize competition will run on Monday afternoon, and there are prizes for the Flash Talks on Wednesday and poster presentations. We are especially grateful to the support provided by our generous sponsors of the meeting. I hope you will have an interesting, challenging and informative time whilst in Glasgow.

Stephen Sproules, *Local Organizer*

### Plenary Speakers

Elena Bagryanskaya  
*Russian Academy of Sciences Novosibirsk, Russia*

Marilena Di Valentin  
*University of Padova, Italy*

Etienne Goovaerts  
*University of Antwerp, Belgium*

David Norman  
*University of Dundee, UK*

### Keynote Speakers

Alice Bowen  
*University of Oxford, UK*

Nicholas Chilton  
*The University of Manchester, UK*

Richard Cogdell  
*University of Glasgow, UK*

David Lurie  
*University of Aberdeen, UK*

Sharon Ruthstein  
*Bar Ilan University, Israel*

Maxim Yulikov  
*ETH Zürich, Switzerland*

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### ESR Spectroscopy Group Committee

Eric McInnes (Chair)  
*The University of Manchester, UK*

Ilya Kuprov (Secretary)  
*University of Southampton, UK*

David Norman (Treasurer)  
*University of Dundee, UK*

Christiane Timmel (Incoming Chair)  
*University of Oxford, UK*

Chris Wedge (Web Master)  
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*Bruker BioSpin GmbH*

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*Universität Bonn, Germany*

Bela Bode  
*University of St Andrews, UK*

Alice Bowen  
*University of Oxford, UK*

Gavin Morley  
*University of Warwick, UK*

Maxie Roessler (2018 Organizer)  
*Imperial College London, UK*

Enrico Salvadori (2018 Organizer)  
*University of Turin, Italy*

SUNDAY 7 <sup>TH</sup> APRIL		
15:00 – 18:00	Registration Check-in	Central Plaza
18:30 – 20:30	Dinner	Waterhouse
20:30 – 00:00	Welcome Reception	Waterhouse and Lounge Bar

MONDAY 8 <sup>TH</sup> APRIL		
07:00 – 09:00	Breakfast	Waterhouse
09:00 – 09:10	Stephen Sproules	Conference Opening
Session Chair: Janet Lovett		Auditorium
09:10 – 09:50 <b>APMR Plenary Lecture</b>	Elena Bagryanskaya	Trityl Radicals as Spin Labels
09:50 – 10:10	Edgar Groenen	Temperature-Cycle Electron Paramagnetic Resonance
10:10 – 10:30	Dinar Abdullin	Pulsed EPR Dipolar Spectroscopy Under the Breakdown of the High- Field Approximation: The High-Spin Iron(III) Case
10:30 – 11:00	Coffee Break	Central Plaza
Session Chair: Etienne Goovaerts		Auditorium
11:00 – 11:30 <b>Keynote Lecture</b>	Maxim Yulikov	Recent Progress in RIDME Spectroscopy with Paramagnetic Metal Ions
11:30 – 11:50	Maria Grazia Concilio	Efficient Treatment of Classical Degrees of Freedom in Magnetic Resonance Simulations
11:50 – 12:10	Sylwia Kacprzak	Sensitivity and Time Resolution in Rapid Scan
International EPR Society – Silver Medal Physics		
12:10 – 12:20	Thomas Prisner	IES Laudatio
12:20 – 12:40 <b>IES Silver Medal</b>	Robert Bittl	Tuning Spin Dynamics in Crystalline Tetracene
12:40 – 14:10	Lunch	Waterhouse

Session Chair: Bela Bode		Auditorium
14:10 – 14:30 <b>JEOL Prize</b>	Anja Elpelt	EPR Spectroscopy for Characterization of Skin Barrier
14:30 – 14:50 <b>JEOL Prize</b>	Frauke Breitgoff	Pushing for Longer Distances: Frequency-Swept Excitation in Distance Measurements of Spin- $1/2$ Systems
14:50 – 15:10 <b>JEOL Prize</b>	Mantas Šimėnas	ESR Spectroscopy of Structural Phase Transitions and Dynamic Effects in Hybrid Metal-Formate Perovskite Frameworks
15:10 – 15:30 <b>JEOL Prize</b>	Andrei Kuzhelev	Room-Temperature EPR Distance Measurements Using Trityl and Nitroxide Spin Labels
15:30 – 16:00	Coffee Break	Central Plaza
16:00 – 17:10	Poster Session	Odd Numbers
Session Chair: Alice Bowen		Auditorium
17:10 – 17:30 <b>JEOL Prize</b>	Nicole Erlenbach	'End-to-End' Stacking of Small dsRNA Studied with PELDOR/DEER
17:30 – 17:50 <b>JEOL Prize</b>	Sonia Chabbra	Application of EPR Methodology Towards Cr/PNP Based Ethylene Tetramerisation Catalysis
17:50 – 18:10 <b>JEOL Prize</b>	Markus Teucher	Gadolinium and Nitroxide Labels to Measure Protein Interactions at Room Temperature with High Field CW EPR and ODNP
18:10 – 18:30 <b>JEOL Prize</b>	Irina Ritsch	Disordered Protein Domains and Distance Measurements by Pulsed EPR - A Match Made in Heaven?
19:00 – 21:00	Dinner	Waterhouse
21:00 – 00:00	JEOL Reception	Central Plaza



TUESDAY 9 <sup>TH</sup> APRIL		
07:00 – 09:00	Breakfast	Waterhouse
Session Chair: Ilya Kuprov		Auditorium
09:00 – 09:40 <b>Plenary Lecture</b>	Etienne Goovaerts	Radical States Involved in the Charge Separation Process and in the Photodegradation of Fullerene-Free Organic Solar Cell Materials
09:40 – 10:00	Luis Fábregas Ibáñez	Hyscorean: Measurement, Processing and Analysis of Non-Uniform Sampled HYSORE
10:00 – 10:20	Vasily Oganessian	Direct Prediction of EPR Spectra from MD Simulations of Lipid Bilayers – a Route to Understanding Structure and Dynamics in Biological Membranes
10:20 – 10:40	Guinevere Mathies	Analysis of the EPR Spectra of Transferrin: The Importance of Zero-Field-Splitting Distributions and 4th-Order Terms
10:40 – 11:10	Coffee Break	Central Plaza
Session Chair: Olav Schiemann		Auditorium
11:10 – 11:40 <b>Keynote Lecture</b>	Sharon Ruthstein	The Tale of the Cellular Copper Cycle
11:40 – 12:00	Maria Fittipaldi	Electric Field Modulation of Magnetic Exchange in Molecular Helices
12:00 – 12:20	Gabriela Ionita	Host-guest Interactions in Polysaccharide Hydrogels Evidenced by Spin Probes
12:20 – 12:40	Mykhailo Azarkh	Gd(III)-Gd(III) RIDME for In-Cell EPR Distance Determination
12:40 – 14:10	Lunch	Waterhouse
14:10 – 17:30	Free Afternoon  Distillery Tour departs at 15:00	
17:30 – 18:30	ESR Group AGM	Auditorium
18:30 – 20:00	Dinner	Waterhouse

Bruker Prize		Auditorium
20:00 – 20:10	Thomas Prisner	Bruker Prize Laudatio
20:10 – 21:00	Marina Bennati	Electron-Nuclear Polarization Transfer in ENDOR and Liquid DNP to Study Biomolecules
21:00 – 00:00	Bruker Reception	Central Plaza

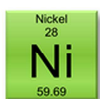
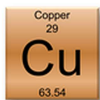
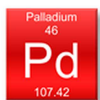
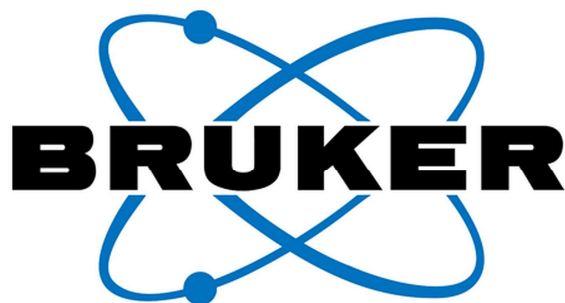
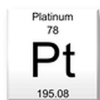
WEDNESDAY 10 <sup>TH</sup> APRIL		
07:00 – 09:00	Breakfast	Waterhouse
MDPI Session Chair: Christiane Timmel		Auditorium
09:00 – 09:40 <b>Plenary Lecture</b>	Marilena Di Valentin	Light-Induced Pulsed EPR Dipolar Spectroscopy: The Triplet State Probe
09:40 – 10:00	Claudia Tait	Twist-Angle Dependence of Triplet State Properties in Twisted Acenes
10:00 – 10:20	Nino Wili	ELDOR-detected NMR: The Curious Case of a Coupled Copper Complex
10:20 – 10:40	Laura Galazzo	'To Each His Own': Spin-Labeled Nanobodies as Proteins' Conformational Reporters
10:40 – 11:10	Coffee Break	Central Plaza
SULSA Session Chair: David Norman		Auditorium
11:10 – 11:40 <b>Keynote Lecture</b>	David Lurie	Imaging Free Radicals Using Field-Cycling Overhauser-Effect MRI
11:40 – 12:00	Christos Pliotas	Mechanical Activation of an Ion Channel Triggered by Modification of Pressure Sensitive Nano-Pockets; a PELDOR, ESEEM and CW-EPR Study
12:00 – 12:30 <b>Keynote Lecture</b>	Richard Cogdell	How Purple Photosynthetic Bacteria Harvest Solar Energy
12:30 – 14:00	Lunch	Waterhouse

EPSRC EPR Service Session Chair: David Collison		Auditorium
14:00 – 14:05	David Collison	EPSRC National UK EPR Facility
14:05 – 14:35 <b>Keynote Lecture</b>	Alice Bowen	A Tasting Menu of Dipolar Spectroscopies
14:35 – 14:55	Gregor Hageleuken	Studying the Conformation of a Receptor Tyrosine Kinase in Solution by Inhibitor-Based Spin Labeling
14:55 – 15:15	Ilya Kuprov	Simulating the Whole of Magnetic Resonance
15:15 – 15:35	Dimitri Svistunenko	Tryptophan Radical EPR Spectra: The $g$ -Values Revised
15:35 – 16:05	Coffee Break	Central Plaza
16:05 – 17:15	Poster Session	Even Numbers
Session Chair: Stephen Sproules		Auditorium
17:15 – 17:25 <b>Flash Talk</b>	Federico Lombardi	Topological Spin-Active Sites in Graphenoid Molecules
17:25 – 17:35 <b>Flash Talk</b>	Jake McGuire	Ligand Radicals as Electron Spin Qubits
17:35 – 17:45 <b>Flash Talk</b>	Laura Esteban Hofer	Characterization of Liquid-Liquid Phase Separation of FUS with EPR Spectroscopy
17:45 – 17:55 <b>Flash Talk</b>	Gabriel Moise	Non-uniform Electronic Delocalisation in the Radical Cations of Porphyrin Molecular Wires
17:55 – 18:00	Live Vote!	
Bruker Thesis Prize		Auditorium
18:00 – 18:10	Graham Smith	Bruker Thesis Prize Laudatio
18:10 – 19:00	Claire Motion	Improving the Sensitivity and Utility of Pulsed Dipolar Experiments in EPR at 94 GHz
19:30 – 00:00	Banquet & Ceilidh	Waterhouse

<b>THURSDAY 11<sup>TH</sup> APRIL</b>		
07:00 – 09:00	Breakfast	Waterhouse
SUPA Session Chair: David Keeble		Auditorium
09:00 – 09:40 <b>Plenary Lecture</b>	David Norman	Multidisciplinary Approaches to Structural Investigation: The Nucleosome its Construction and its Remodeling
09:40 – 10:00	Rachel Haywood	Interaction Between 694 nm Red (Ruby) Laser Photons and a Static Magnetic Field – Evidence for Charge and Therefore Photon Mass?
10:00 – 10:20	Christopher Wedge	Exploiting Radical Triplet Pair Hyperpolarization: Sensitivity Enhancement in Solution-State NMR
10:20 – 10:40	Janet Lovett	A Gadolinium Spin Label with Both a Narrow Central Transition and Short Tether for Use in Double Electron Electron Resonance Distance Measurements
10:40 – 11:05	Coffee Break	Central Plaza
ScotCHEM Session Chair: Eric McInnes		Auditorium
11:05 – 11:10	Bill MacDonald	ScotCHEM
11:10 – 11:40 <b>Keynote Lecture</b>	Nicholas Chilton	Measurement of Magnetic Exchange in Asymmetric Lanthanide Dimetallics
11:40 – 12:00	Leah Weiss	Correlating Exciton Localization and Diffusion with Intermolecular Structure Using Spin Resonance in an Organic Semiconductor
12:00 – 12:20	Bela Bode	Quantitative Pulse Dipolar EPR at Submicromolar Concentration Reveals Submicromolar Cu <sup>II</sup> -Affinity of Double Histidine Sites in Proteins
12:20 – 12:40	Michal Zalibera	EPR Insights into the Molecular Gripping Machinery
12:40 – 12:45	Eric McInnes	2020 Meeting Announcement
12:45 – 14:15	Lunch	Waterhouse
14:15	Departure	

## Sponsors

We are indebted to the following sponsors for their generous support





The ESR Spectroscopy Group of the Royal Society of Chemistry is pleased to announce the 22<sup>nd</sup> JEOL Prize Talk, sponsored by JEOL. The competition is open to any doctoral student (typically in year 2 or beyond) and 1<sup>st</sup> year postdoctoral scientists. The 15 minute lectures will be judged by the ESR Group Committee on the basis of both scientific content and delivery. The competition is scheduled for Monday afternoon and will be followed that evening with the JEOL Reception. The winner will be announced at the Banquet on Wednesday evening.

The following eight lectures were selected by the committee on the basis of the abstracts submitted:

<b>Anja Elpelt</b> Freie Universität Berlin	EPR Spectroscopy for Characterization of Skin Barrier
<b>Frauke Breitgoff</b> ETH Zürich	Pushing for Longer Distances: Frequency-Swept Excitation in Distance Measurements of Spin- <sup>1</sup> / <sub>2</sub> Systems
<b>Mantas Šimėnas</b> Vilnius University	ESR Spectroscopy of Structural Phase Transitions and Dynamic Effects in Hybrid Metal-Formate Perovskite Frameworks
<b>Andrei Kuzhelev</b> Russian Academy of Sciences Novosibirsk	Room Temperature EPR Distance Measurements using Trityl and Nitroxide Spin Labels
<b>Nicole Erlenbach</b> Goethe Universität Frankfurt	'End-to-End' Stacking of Small dsRNA Studied with PELDOR/DEER
<b>Sonia Chabbra</b> MPI für Chemische Energiekonversion	Application of EPR Methodology toward Cr/PNP-Based Ethylene Tetramerisation Catalysis
<b>Markus Teucher</b> Ruhr-Universität Bochum	Gadolinium and Nitroxide Labels to Measure Protein Interactions at Room Temperature with High Field cw EPR and ODNP
<b>Irina Ritsch</b> ETH Zürich	Disordered Protein Domains and Distance Measurements by Pulsed EPR - A Match Made in Heaven?

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#### Previous winners of the JEOL Student Prize

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

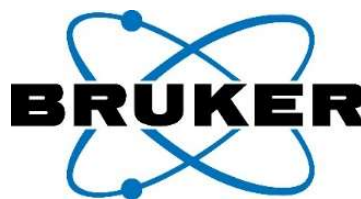
## Bruker Prize

Since 1986 Bruker BioSpin has generously sponsored an annual lectureship and prize, given to a scientist who has made a major contribution to the application of ESR spectroscopy in chemical or biological systems. The ESR Spectroscopy Group of the Royal Society of Chemistry is pleased to announce that the 2019 Bruker Prize will be awarded to:



### Professor Marina Bennati

*MPI für biophysikalische Chemie*



As the nominations highlighted her outstanding work spans not just ESR but also the neighbouring disciplines of NMR and DNP. Even within EPR the scope of her work is large and impressive including both state of the art ESR methods applied to biophysics, instrumental development (e.g. dual mode cavity for W-band, rapid freeze quench for multi-frequency ESR) and theoretical accounts of the results (e.g. CP-ENDOR and orientation selection).

Professor Bennati will deliver the 2019 Bruker lecture entitled:

***Electron-Nuclear Polarization Transfer in ENDOR and Liquid DNP to Study Biomolecules***

on Tuesday 9<sup>th</sup> April commencing at 20:00. The will be followed by the Wine Reception also kindly sponsored by Bruker BioSpin.

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#### Previous winners of the Bruker Prize

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



## Bruker Thesis Prize

The ESR Spectroscopy Group of the Royal Society of Chemistry and the Bruker Corporation established the Bruker Thesis Prize to recognise outstanding work by PhD students in the field of ESR spectroscopy. The 2019 recipient is **Claire Motion** for her thesis completed at the University of St Andrews. Our expert panel of reviewers said of her work:

*“Dr Motion has significantly enhanced sensitivity of a cutting-edge spectrometer and has demonstrated an incredible sensitivity improvement in low-spin Fe(III)-nitroxide DEER, which no expert would have predicted. This was not just a matter of luck, but a result of meticulous preparation and deep understanding. [...] the thesis of Dr Motion is a convincing demonstration of scholarship [...] it is very impressive how many journal articles she managed to publish.”*



Dr Motion will deliver the 2019 Bruker Thesis Prize lecture entitled:

***Improving the Sensitivity and Utility of Pulsed Dipolar Experiments in EPR at 94 GHz***

at a session starting at 18:00 on Wednesday 10<sup>th</sup> April.

### Previous winners of the Bruker Thesis Prize

2015 Joshua Biller, University of Denver

2017 Andrin Doll, ETH Zürich

2016 Claudia Tait, University of Oxford

2018 Audrey Bienfait, CEA-Saclay



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## Poster Prizes

The RSC ESR Group are delighted to announce that in total five poster prizes will be awarded to the best poster presentations by young researchers at the 52<sup>nd</sup> Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry. All posters presented by young researchers at the conference will automatically be considered for these prizes

These poster prizes are generously provided by:



The Royal Society of Chemistry has provided a copy of the latest *Specialist Periodical Reports in Electron Paramagnetic Resonance*, Volume 26 (2019).



The International EPR (ESR) Society will sponsor two one-year free IES memberships.



These will include two RSC publishing book vouchers provided by the flagship journals of the Royal Society of Chemistry.



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

<b>Elena Zaytseva</b>	Hybrid Phenoxyl-Nitroxide Radicals as a New Building Block in Magnetochemistry	P1
<b>Nino Wili</b>	ELDOR-detected NMR: The Curious Case of a Coupled Copper Complex	P2
<b>Luis Fábregas</b>	Hyscorean: Measurement, Processing and Analysis of Non-Uniform Sampled HYSCORE	P3
<b>Mario Winkler</b>	The Static and Dynamic Electronic and Geometric Structure of Catalysts in Mesoporous Polymers	P4
<b>Dennis Schäfer</b>	Novel Potential Multi-Qubit Systems with Very Rigid Bridging Ligands	P5
<b>Anna Rubailo</b>	DEER Measurement Employing for Exploring the Binding Site of Fucose-Functionalized Precision Glycomacromolecules Targeting Human Norovirus Capsid Protein	P6
<b>Fabian Hecker</b>	$^{17}\text{O}$ High Field ENDOR to Investigate Water-Mediated PCET in E.coli Ribonucleotide Reductase	P7
<b>Andreas Scherer</b>	Theoretical Inspection of Laser-Induced Magnetic Dipole Spectroscopy (LaserIMD)	P8
<b>Hasan Alniss</b>	Biophysics in Drug Discovery: Characterization of Ligand-DNA Interactions by NMR Spectroscopy and Isothermal Titration Calorimetry	P9
<b>Jūras Banys</b>	ESR Spectroscopy of Structural Phase Transition in $\text{Mn}^{2+}$ Doped $[(\text{CH}_3)_2\text{NH}_2][\text{Cd}(\text{N}_3)_3]$ Hybrid Perovskite Framework	P10
<b>Daniel Klose</b>	EPR and Hyperfine Spectroscopy Study of the Metallochaperones Assisting the $\text{Cu}_A$ Center Assembly on Cytochrome Oxidase	P11
<b>Maria Oranges</b>	Multi Frequency Orientation Selective Copper(II) Nitroxide RIDME in Model Systems and Proteins	P12
<b>Irina Ritsch</b>	Disordered Protein Domains and Distance Measurements by Pulsed EPR - A Match Made in Heaven?	P13
<b>Iulia Matei</b>	Processes Mediated by Encapsulated AuNP in Polymeric Gels Evidenced by EPR Spectroscopy	P14
<b>Arnau Bertran</b>	Evolution of Free Radicals from a Novel Pt(IV) Mono Azido Complex Following Irradiation with Visible Light	P15
<b>Denisa Darvasiová</b>	<i>In-situ</i> EPR/UV-Vis-NIR Spectroelectrochemistry of Thienoacene-Extended Tetrathiafulvalenes	P16

Miriama Šimunková	Prospective Copper(II) Metallodrugs with Redox Cycling and Intercalating Functionalities	P17
Zuzana Barbieriková	EPR Spin Trapping Technique as a Useful but Tricky Tool in the Studies of Photoinduced Processes	P18
Gert Denninger	ESR: A Non-Invasive Technique for Quality Control in Carbon Fibre Production and the Characterisation of Carbon Fibre Products?	P19
Janne Soetbeer	Waterproofing Dynamical Decoupling: Nitroxides in H <sub>2</sub> O:Glycerol Glasses	P20
Jacob Pullin	Free Radical Formation in H <sub>2</sub> O <sub>2</sub> -Driven Iron Oxidation by Bacterioferritin	P21
Ashley Redman	Triplet states of Donor-Acceptor Substituted Porphyrins	P22
Benjamin Tucker	An Investigation of Refocused Out of Phase DEER and RIDME	P23
Graham Smith	High Field Orientationally Selective Multi-Spin PELDOR – What is going on?	P24
Vinicius Santana	Magnetic-Field-Tuned Phase Transition of a Copper Compound from the Isolated-Spin to the Coupled-Spin Regime Probed by EPR	P25
Jakub Hrubý	Spectroscopy of High-Spin Co(II) Single-Molecule Magnet	P26
Liam Trzaska	Electron Paramagnetic Resonance of Fe <sup>3+</sup> in BaTiO <sub>3</sub>	P27
Ronan Fisher	Conformational Changes in the Structure of Human Calmodulin in a Calcium-Substrate Dependent Manner	P28
Michael Taylor	Pulsed EPR Investigation of Metal Binding to Coiled-Coil Peptides	P29
Agathe Vanas	EPR Characterisation of Trityl Radicals with the Finland Trityl Radical Scaffold and Two Orthogonal Functional Groups	P30
William Myers	<i>CH</i> irped, <i>OR</i> dered Pulses for <i>U</i> ltra-Broadband [ESR] Spectroscopy	P31
Rémi Blinder	Optically-induced Dynamical Nuclear Polarization in Diamond Materials	P32

## Practical Information

### Registration

Registration for all conference attendees will open at 15:00 on Sunday from 15:00 to 18:00 at the registration desk in the hotel lobby. You will receive your registration pack and room key, and can provide details to the hotel to have extra items charged directly to the room. For attendees arriving later than this can check-in at the hotel reception and join us in The Waterhouse for dinner or the adjacent bar/lounge for the evening reception. On all other days, conference registration will be open for day registration between 8:30 and 9:00 am, and the morning coffee breaks. Please see a member of the organizing team.

### Accommodation and Meals

All participants will be accommodated in the Golden Jubilee Conference Hotel. The hotel is equipped with a gym, steam room, sauna and indoor pool which is open to all hotel guests. All meals are served in The Waterhouse located on the ground floor. The exact times for lunches and dinners vary slightly from day to day depending on the program – see the conference book for details. Please note that Lunch is included in the cost of all registrations. Breakfast and dinner are included for all participants with accommodation, but must be booked separately for day participants. If any day participants would like to register for any additional dinners during the conference, please speak to a member of the local organizing team.

### Lectures

All lectures will be held in the Auditorium on the ground floor of the hotel, off from the Central Plaza. Morning sessions start at 9:00 am Monday to Thursday.

### Speaker Information

Please allow 5 minutes for discussion at the end of all lectures. Excluding discussion time, keynote lectures will be 35 minutes, invited lectures 25 minutes, and contributed lectures and JEOL Student Prize talks 15 minutes. Flash Talks are 8 minutes in duration with a 2 minute discussion period at the end. A Windows PC with PowerPoint 2016, Adobe Reader and a projector will be provided. When saving your PowerPoint file for the presentation, please make sure that:

1. All fonts have been embedded (tick the relevant box in the file saving options).
2. All externally linked graphics and video files are present in the same directory as the presentation file. The best way of doing that is to use the “Export/Package for CD” option.

Speakers are kindly asked to upload their presentations onto this computer (and set up and test them) in the morning before the first session of the day of their presentation. It will also be possible to attach speaker's own laptop to the projector. If it is strictly necessary, speakers may use their own laptops, but we discourage this in order to minimise the switch-over time between presentations and you must provide any required display adapter. Members of the local organising team will be available to open the Auditorium and provide limited assistance. Please would all speakers ensure they keep strictly to the time schedule for their talk.

### Poster Presenter Information

Poster sessions will take place on Monday afternoon (odd numbers) and Wednesday afternoon (even numbers) in the Central Plaza which is also contains the hotel reception and connects to the Auditorium. Poster boards are A0 in size (portrait and landscape) and should be setup on Sunday before 18:00 or Monday morning before the poster session begins; they will have to be taken down on Thursday morning. Velcro stickers to attach the posters to the boards will be provided. Poster numbers will be displayed on the boards. The posters will be on display throughout the conference, and coffee breaks/receptions will be held near the posters.

### Coffee Breaks

Tea, coffee and refreshments will be served during the morning and afternoon breaks and the poster sessions in the Central Plaza.

### Conference Banquet

The conference banquet will take place on Wednesday, April 10 at 19:30 in The Waterhouse. In accordance with Scottish tradition, the banquet will be followed by a traditional Ceilidh led by the committee chair.

### Accompanying Persons

Although there is no formal program of events for accompanying persons, the conference organizers will be happy to suggest interesting places to visit both within Glasgow itself and the surrounding area. Useful tourist information can be found at [peoplemakeglasgow.com](http://peoplemakeglasgow.com). Any queries relating to the hotel facilities should in the first instance be addressed to the reception desk. For matters relating to the conference, please ask any member of the organizing team.

### Internet Access

WiFi is available throughout the hotel. Instructions on how to connect to the network will be inserted in the conference bags. Hard wired internet access can also be provided in bedrooms but will require an Ethernet cable.

### Shop

The Golden Jubilee Hospital has a small shop for sundry items that is open week days until 8 pm. The shop also has an ATM and is along the corridor following the signs from the Central Plaza.

### Departure

Participants should vacate their room by 12:00 pm on Thursday, April 11. Luggage storage is provided until the end of the conference, which concludes after lunch on the final day.



## Social Program

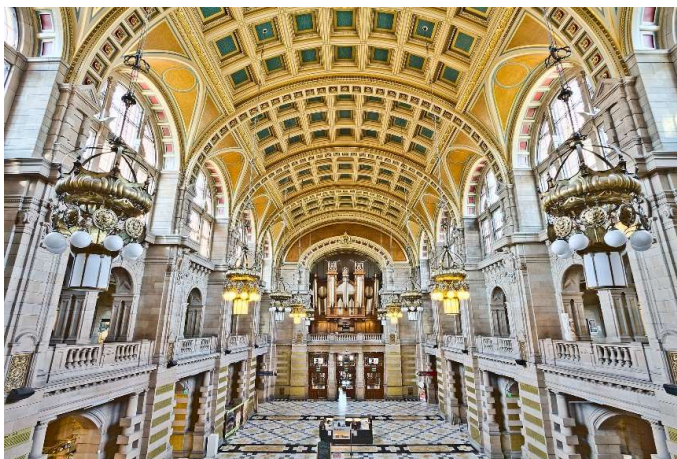
### Whisky Distillery Tour

No trip to Scotland is complete without visit to one of its world famous whisky distilleries. *Auchentoshan*, which translates from Gaelic as “corner of the field”, is located just 1.7 miles (2.7 km) from the conference hotel. Described as Glasgow’s malt whisky, it is the only distillery out of more than 100 to practice triple distillation. The guided tour of the distillery lasts an hour and concludes with the compulsory sampling of one of their signature single malts and a whisky cocktail. The coach will depart from outside the hotel promptly at 15:00; the first group of 30 will commence their tour at 15:20, with the second group following 15 minutes later. The tour party will return to the coach by 16:45 for the journey to the hotel.



### Glasgow

The free afternoon will give the participants the opportunity to explore Glasgow that is home to a wealth of cultural attractions, impressive architecture, fantastic shopping and a year-round programme of world-class events. Frequent trains from Dalmeir take 25 minutes to reach Glasgow Central at a cost of £3.90 return. For those wishing to explore Glasgow on their own, maps of the city centre and directions on how to reach specific locations can be provided by the conference team after your arrival.



### Wine Receptions and Conference Banquet

There will be three evening drink receptions during the course of the conference. A reception will follow dinner on Sunday evening, kindly sponsored by the ESR Spectroscopy Group of the RSC. On Monday, the JEOL Student Prize competition will culminate in a wine reception sponsored by JEOL, and the Bruker Prize winners will be toasted at the Bruker wine reception following on Tuesday evening.

The conference banquet will be held in The Waterhouse on Wednesday, April 10 at 7:30 pm, and be followed by a Ceilidh.

## Travel Information

The Golden Jubilee Conference Hotel is located 8 miles (13 km) west of Glasgow in Clydebank. There are several ways of travelling here as detailed below. Please do not hesitate to ask us for any advice or guidance on getting to and around Glasgow.

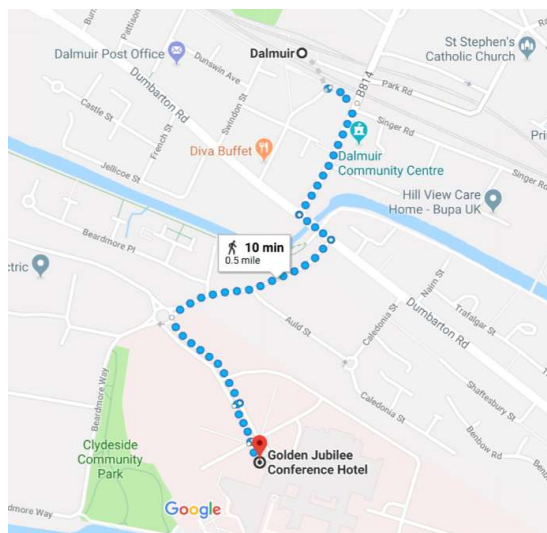
### By plane

Glasgow is serviced by two airports. The larger of the two is Glasgow Airport (GLA) a mere 20 minute drive from the conference venue. With over 100 destinations, there are direct flights from many major cities across the British Isles and Europe. In addition there are daily connections to major hubs on the eastern seaboard of the United States and Canada. There is a complimentary shuttle service in both directions between the hotel and the airport. Those entering through Glasgow airport will need to provide their arrival and departure details to the local organizers.

The smaller Glasgow Prestwick Airport (PIK) is located 35 miles (56 km) south of the city on the west coast. It is serviced by various low cost carriers from 16 destinations across Europe. A train from the airport will take 45 minutes to bring you to Glasgow Central station. Alternatively the X77 is an express service to Glasgow Buchanan Street bus station. A private taxi will set you back £49 for the journey.

### By train

Glasgow Central station is entry point northbound trains from England along the West Coast mainline. Westbound trains from various points in Scotland and north east England arrive in to Glasgow Queens Street station. The conference venue is a short 10 minute walk from Dalmuir station. Those arriving by train are reminded to purchase a ticket to Dalmuir and change at one of the major stations in the city centre so there is no need to purchase additional tickets. For further information please visit [www.nationalrail.co.uk](http://www.nationalrail.co.uk)



### By coach

Buchanan Bus Station is the main terminus for long distance coaches and is close to Buchanan Street subway station. Timetables at [www.travelinescotland.com](http://www.travelinescotland.com)

### By car

Motorway links provide access from major UK cities to the Golden Jubilee Conference Hotel. The formal address is: Beardmore Street, Clydebank, Glasgow, G81 4SA (WH4C+JW Clydebank). From Carlisle, Newcastle and the South, exit M74 on to the M73, joining the M8 at the Old Monkland junction. Edinburgh and east of Scotland drivers also use the M8 until exit 19 and follow signs for Clydebank/A814. Continuing west on the expressway it will eventually become Dumbarton Road bringing you to the Golden Jubilee hotel. Ample parking is available.

TALK  
ABSTRACTS



## Trityl Radicals as Spin Labels

Elena Bagryanskaya<sup>1,2</sup> and Olesya Krumkacheva<sup>1,2,3</sup>

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In recent years, the combination of dipolar EPR spectroscopy with site-directed spin labeling (SDSL) has become a powerful method to study tertiary structure, dynamics and functional features of proteins, nucleic acids and nucleoproteins. Trityl radicals or TAMs have appeared recently as an alternative source of spin labels for measuring long distances in biological systems.<sup>[1]</sup>

In this presentation the advantages of spin labels based on TAM radicals will be shown of following examples:

- (i) Investigation of the conformational changes of DNA with the apurinic/apyrimidinic sites (abasic or AP sites), which are one of the most common DNA lesions site and structure of DNA complexes with human apurinic/apyrimidinic endonuclease 1.<sup>[2]</sup>
- (ii) Development of spin labels based on the very hydrophilic OX063 with very-low toxicity and little tendency for aggregation. These new spin labels were tested on human serum albumin (HSA) as one of the most abundant protein in blood plasma.<sup>[3]</sup>
- (iii) Development of C<sub>60</sub>-based label for dipolar EPR spectroscopy using model covalent pairs of C<sub>60</sub> with trityl (C<sub>60</sub>-TAM) radicals having long phase relaxation time up to room temperature.<sup>[4]</sup>
- (iv) Synthesis of novel TAM-nitroxyl biradicals of different structure and their application as DNP agent.<sup>[5]</sup>

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[1] O. Krumkacheva and E. Bagryanskaya, in *Electron Paramagnetic Resonance*, ed. V. Chechik and D. M. Murphy, The Royal Society of Chemistry, Cambridge, UK, 2017, vol. 25, p. 35.

[2] O. A. Krumkacheva, G. Shevelev, A. Lomzov, N. Dyrkheeva, A. A. Kuzhelev, V. V. Koval, V. M. Tormyshev, I. Kirilyuk, M. Fedin, D. Pyshnyi, O. Lavrik and E. G. Bagryanskaya, *Nucleic Acids Res.*, 2019, submitted.

[3] V. M. Tormyshev, O. A. Krumkacheva, A. Chubarov, D. V. Trukhin, O. Yu. Rogozhnikova, A. Spitsina, A. A. Kuzhelev, V. V. Koval, M. Fedin, T. Godovikova, M. Bowman and E.G. Bagryanskaya, *Chem. Eur. J.*, 2019, submitted.

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[5] S. Bothe, J. Nowag, V. Klimavicius, M. M. Hoffmann, T. I. Troitskaya, E. V. Amosov, V. M. Tormyshev, I. Kirilyuk, A. Taratayko, A. A. Kuzhelev, D. Parkhomenko, E. G. Bagryanskaya, T. Gutmann and G. Buntkowsky, *J. Phys. Chem. C*, 2018, **122**, 11422.

## Temperature-Cycle Electron Paramagnetic Resonance

E. Gabriele Panarelli, Peter Gast and Edgar J. J. Groenen

*Department of Physics, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands*

We introduce a novel approach to the study of rates and short-lived intermediates of reactions that involve paramagnetic species. Temperature-cycle EPR concerns the repeated heating of the sample in the EPR cavity by pulsed irradiation with a near-infrared laser combined with intermittent EPR investigation at 275 GHz of the sample at a lower temperature where the reaction does not proceed during the measurement. The new technique is demonstrated for the reduction of TEMPOL by sodium dithionite in buffered aqueous solution. We introduce a simple way to load an unreacted sample in the EPR spectrometer at low temperature and show that one sample suffices to obtain a complete kinetic trace. Variation of the length and power of the laser pulse offers great flexibility as regards the time scale of the experiment and the temperature at which the reaction can be studied.

We present sub-second time resolution and show that analysis of the temperature development of the sample during the infrared laser pulse allows a quantitative description of the reduction of TEMPOL in terms of reaction rate and activation energy.

## Pulsed EPR Dipolar Spectroscopy Under the Breakdown of the High-Field Approximation: The High-Spin Iron(III) Case

Dinar Abdullin,<sup>1</sup> Hideto Matsuoka,<sup>1,2</sup> Maxim Yulikov,<sup>3</sup> Nico Fleck,<sup>1</sup> Christoph Klein,<sup>1,4</sup> Sebastian Spicher,<sup>5</sup> Gregor Hagelueken,<sup>1</sup> Stefan Grimme,<sup>5</sup> Arne Lützen<sup>4</sup> and Olav Schiemann<sup>1</sup>

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<sup>5</sup> Mulliken Center for Theoretical Chemistry, University of Bonn, Bonn, Germany

Pulsed EPR dipolar spectroscopy (PDS) is a valuable method to acquire nanometer distance constraints for the characterization of biomolecular structures and their conformational changes during function. In the case of diamagnetic biomolecules, PDS measurements require the site-specific labeling of a bio-molecule with two spin labels. When a biomolecule contains an intrinsic paramagnetic metal center, PDS can be applied to determine the distance between such a metal center and a single spin label. The latter case allows to reduce the number of spin labels and, consequently, the number of protein mutations, as well as it enables the localization of metal ions within the protein fold via trilateration<sup>1</sup> and the docking of different parts of protein complexes using metal ions as anchor points.<sup>2</sup> Up to now, PDS measurements were applied only to those metal centers that adhere to the high-field approximation, meaning that the zero-field splitting (ZFS) of these centers is much smaller than the Zeeman interaction.<sup>3</sup> The application of PDS to other metal centers, for which the high-field approximation breaks down, is still very challenging and has not been explicitly considered so far. In the present report, it will be shown how the theory of the dipole-dipole interaction and the PDS methodology can be extended to the latter case on example of a high-spin Fe<sup>3+</sup>/nitroxide spin-pair.

The theoretical consideration of the high-spin Fe<sup>3+</sup>/nitroxide spin-pair revealed that the corresponding dipolar spectrum depends not only the inter-spin distance and the angle between the distance vector and the applied magnetic field, but also on the orientation of the distance vector with respect to the effective g-tensor of the Fe<sup>3+</sup> ion. This prediction was validated experimentally for two test systems, a porphyrin model compound and a spin-labelled heme protein met-myoglobin. The dipolar spectra of both test systems were acquired by means of a PDS method called relaxation induced dipolar modulation enhancement (RIDME). The parameters of the RIDME experiment were optimized in accordance to the relaxation behavior of the high-spin Fe<sup>3+</sup> ions. To extract the distance and angular distributions from the RIDME spectra, a new data analysis program was developed and successfully applied to the RIDME data of both test systems. The accuracy of the obtained distance and angular distributions was confirmed by comparing them to the results of the molecular modelling. Taken together, the results of the present report lay the foundation for further applications of PDS to the spin systems with large ZFS, e.g., the highly relevant class high-spin Fe(III) heme proteins.

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## Recent Progress in RIDME Spectroscopy with Paramagnetic Metal Ions

Maxim Yulikov

*Department of Chemistry and Applied Bioscience, ETH Zurich, Vladimir Prelog Weg, 2, 8093, Zurich, Switzerland*

Relaxation Induced Dipolar Modulation Enhancement (RIDME) is a pump-probe type of pulse EPR technique, with quite some similarities to the well-known DEER/PELDOR method.<sup>[1,2]</sup> RIDME as well as DEER belong to the so-called Pulse Dipolar Spectroscopy (PDS) techniques, which are most broadly applied to study bio-macromolecule's structures and conformational changes. In the case of RIDME technique the "pump excitation" happens spontaneously, due to the stochastic flips of the partner spins in the dipolar-coupled spin pairs, while in the DEER technique the pump excitation is achieved by applying a microwave pulse. The RIDME technique is of importance for studies of magnetic dipolar interactions in the spin pairs, where at least one of the two coupled paramagnetic centers has so broad EPR spectrum that its full excitation by a microwave pulse is difficult to achieve with currently available setups. Over the last few years, there was a large number of works, mainly focused on RIDME measurements in spin pairs consisting of two paramagnetic metal ions, or a paramagnetic metal ion and an organic radical.

Here we will report our own most recent work devoted to understanding of the basic properties of the RIDME experiment in the metal-metal and metal-nitroxide spin pairs. The first block of topics will encompass different types of artefacts which might appear in the RIDME measurements. To this respect, we will talk about echo crossing artefacts, background correction artefacts, and orientation averaging. In relation to the last point, we will briefly demonstrate the 2D version of RIDME experiment, useful for both orientation averaging and orientation selection analysis. The second block will be devoted to the RIDME background properties, which depend on electron-electron and electron-nuclear spin-spin interactions. We will discuss the changes in the RIDME background shape due to the inter-pulse delay settings, type of the matrix, spin label concentration, temperature, and matrix inhomogeneity in the local vicinity of the detected spins. In the third block we will discuss the particular features of the RIDME experiments with high-spin metal centers. Lastly, we will mention some recent applications of the RIDME technique in our lab.

The work is supported by SNSF (Grant 200020 157034).

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## Efficient Treatment of Classical Degrees of Freedom in Magnetic Resonance Simulations

Ahmed Allami, Maria Grazia Concilio and Ilya Kuprov

*School of Chemistry, University of Southampton, Highfield Campus, Southampton SO17 1BJ, UK*

We propose a solution to the matrix dimension problem in quantum mechanical simulations of magnetic resonance experiments involving multiple classical degrees of freedom – diffusion, flow, microwave phase, rotor phase, *etc.* This problem is very old; it arises when direct products of spin operators and spatial dynamics generators are taken – the resulting matrices are too big for any current or future computer. Mathematically speaking, the structure of the problem is:

$$[\text{space dynamics}] \otimes [\text{reaction kinetics}] \otimes [\text{spin dynamics}]$$

with the equation of motion consequently having the following general form:

$$\frac{d}{dt} \mathbf{\rho}(t) = \left[ \sum_{nmk} a_{nmk}(t) \mathbf{M}_n \otimes \mathbf{K}_m \otimes \mathbf{S}_k \right] \mathbf{\rho}(t)$$

where  $\mathbf{\rho}$  is the state vector,  $a_{nmk}$  are interaction amplitudes,  $\mathbf{M}_n$  are spatial operators,  $\mathbf{K}_m$  are chemical kinetics operators, and  $\mathbf{S}_k$  are spin superoperators. The problem of simulating each of the three compartments individually is comprehensively solved and extensively studied. However, the composite problem runs into the matrix dimension issue: for 3D samples, matrix dimensions in the composite problem routinely exceed  $10^{12}$ .

However,  $\{\mathbf{M}_n, \mathbf{K}_m, \mathbf{S}_k\}$  individually have manageable dimensions, and we note that the action by their direct products on a vector may be computed without opening the products, *e.g.*

$$[\mathbf{A} \otimes \mathbf{B}] \mathbf{v} = \text{vec}[\mathbf{B} \mathbf{V} \mathbf{A}^T]$$

where  $\mathbf{A}$  and  $\mathbf{B}$  are matrices,  $\mathbf{v}$  is a vector,  $\mathbf{V}$  is obtained by reshaping  $\mathbf{v}$  into appropriate dimensions for the product on the right hand side, and *vec* stands for a column-wise stretch back into a vector. The right-hand side is massively easier to compute. The entire class of such relations is well researched; they extend to multiple and nested direct products, and their sums.

We postulate here that direct products are best left unopened in magnetic resonance simulations, particularly in MRI, where the most problematic product is between spatial and spin degrees of freedom. This hypothesis is explored in this work: we report the design and implementation of a spatio-temporal magnetic resonance module in *Spinach v2.4* that uses polyadics (the formal name for a sum of direct products) without opening them.<sup>[1]</sup> This eliminates large matrices from the simulation process. It is demonstrated that previously unthinkable simulations involving classical degrees of freedom now run in minutes.<sup>[2]</sup>

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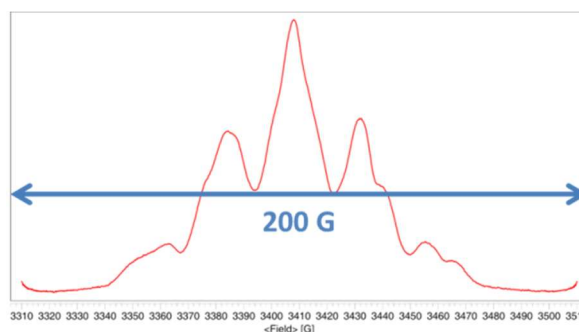
## Sensitivity and Time Resolution in Rapid Scan

Sylvia Kacprzak

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Higher sensitivity and shorter acquisition times are aspects drawing attention to the recently developed Rapid Scan (RS) EPR technique.<sup>[1]</sup> In RS-EPR, the EPR absorption spectrum up to a width of 200 G can be acquired on a time scale of microseconds. Due to the short time during which the spins are exposed to microwave field, the saturation effect is less pronounced compared to conventional continuous-wave EPR. Thus higher microwave fields can be used to increase the signal amplitude. In addition, Rapid Scan provides the opportunity for unprecedented levels of time resolution while collecting the EPR spectrum for following reaction kinetics by continuous-wave techniques.

The Direct Rapid Scan (DRS) EPR Accessory designed by Bruker further extends the functionality and performance of ELEXSYS and EMX series. The configuration of the DRS Accessory and its performance will be discussed with a focus on experiments illustrating both sensitivity and time resolution.



**Figure 1.** Rapid Scan spectrum of gamma irradiated

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## Tuning Spin Dynamics in Crystalline Tetracene

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<sup>1</sup> Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, D-14195 Berlin, Germany

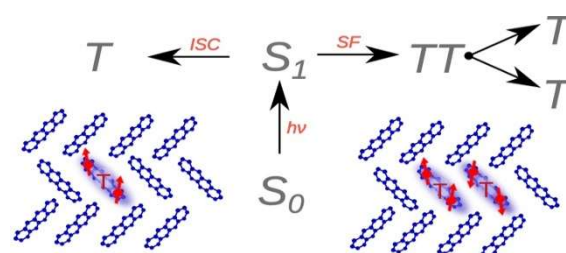
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<sup>3</sup> National Laboratory of Solid State Microstructures, School of Physics, Nanjing University, Nanjing 210093, China

<sup>4</sup> Synergetic Innovation Center in Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

<sup>†</sup> Contributed equally to this work

Tetracene is the archetypal material undergoing singlet fission - the generation of a pair of triplet excitons from one singlet exciton. Here, using time-resolved EPR, we show how the spin dynamics in tetracene crystals are influenced by temperature and morphology. On cooling from 300 to 200 K, we observe a switch between singlet fission and intersystem crossing generated triplets, manifesting as an inversion in transient spin polarization. We extract a spin dephasing time of approximately 40 ns for fission-generated triplets at room temperature, nearly 100 times shorter than the dephasing time we measure for triplets localized on isolated tetracene molecules doped into the host paraterphenyl. These results highlight the strength of time-resolved EPR to unravel the parameters important for efficient singlet fission systems.



**Figure 1.** Tuning spin dynamics in tetracene. In single crystal tetracene at room temperature, singlet fission can generate pairs of spin-polarized triplets ( $TT$ ) from an initial singlet exciton ( $S_1$ ), photogenerated from the singlet ground state ( $S_0$ ) by a photon of energy  $h\nu$ . By lowering the temperature, or preventing in- termolecular coupling, intersystem crossing can instead become the dominant triplet-generation mechanism, generating a single triplet ( $T$ ) from the initial singlet state.

We acknowledge support from DFG SPP-1601 (BI 464/10-2, BE 5126/1-2) and the Nanoscale project within the excellence initiative of the Freie Universität Berlin. The work at Nanjing University is supported by the National Natural Science Foundation of China (21873047). We thank L. R. Weiss for insightful discussions.



## EPR Spectroscopy for Characterization of Skin Barrier

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<sup>4</sup> Department of Physics, Institute of Experimental Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

<sup>5</sup> Institute of Pharmacy, Department of Pharmaceutical Technology, Freie Universität Berlin, Kelchstraße 31, 12169 Berlin, Germany

Electron paramagnetic resonance (EPR) spectroscopy has a wide range of applications, *e.g.* in dermatology.<sup>[1]</sup> One of them is the investigation of the polarity of microenvironment to study bio- and artificial membranes as well as drug localization within delivery systems.<sup>[2,3]</sup> In this study, *ex vivo* human abdominal and breast skin, *ex vivo* porcine abdominal and ear skin as well as normal and inflammatory *in vitro* skin equivalents were analyzed. X-band EPR measurements have shown that the spin probe TEMPO partitions in the lipophilic and hydrophilic microenvironment in varying ratios in different *ex vivo* and *in vitro* skin models. The lowest amount of TEMPO in the lipophilic microenvironment (25%) was determined in *ex vivo* human breast skin and the inflammatory *in vitro* skin equivalent by EPR spectra simulation. In contrast, *ex vivo* human abdominal skin exhibited the highest amount of TEMPO (54%) in the lipophilic microenvironment. To assess the meaning of these results, we investigated the main characteristics of the stratum corneum, the uppermost skin layer and the most lipophilic part of the skin tissue: thickness (histology), lipid composition (HPTLC) and lipid chain order (ATR-FTIR). The lipophilic part of the TEMPO partitioning mostly correlated with the thickness of the stratum corneum and to a lesser degree with the lipid chain order. However, no correlation in the lipid composition was observed. We suggest, that EPR spectroscopy could be utilized as a novel technique to detect differences in the thickness of the stratum corneum, which represents the main skin barrier.

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## Pushing for Longer Distances: Frequency-Swept Excitation in Distance Measurements of Spin- $1/2$ Systems

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*Laboratory of Physical Chemistry, ETH Zürich, Vladimir Prelog Weg 2, 8093 Zürich, Switzerland*

Many projects aimed at the structural characterization of biological macromolecules rely on long-range distance restraints.<sup>[1]</sup> Typically used methods are Double Electron Electron Resonance (DEER) and fluorescence spectroscopy, specifically Förster Resonance Energy Transfer (FRET). Sensitivity in many cases restricts applications, in particular the upper distance limit of 5–16 nm which depends on the system in EPR. Furthermore, the angular dependence of the dipolar coupling can introduce uncertainty in the distance extraction, an effect called *orientation selection*.

Implementation of broadband frequency-swept (chirp) excitation to EPR became possible only a few years ago and has already allowed for improvement of pulse sequences as well as the development of new techniques.<sup>[2,3]</sup> For example, chirp pulses have been shown to increase the modulation depth of Single Frequency TEchnique for Refocusing (SIFTER) measurements drastically.<sup>[4]</sup> They enable correlation of the dipolar and EPR spectrum,<sup>[5]</sup> which in turn allows analysis of the relative orientation of spin centers.<sup>[6]</sup>

Here, the use of frequency-swept pulses in sequences for distance measurement will be discussed. To avoid complications due to high-spin effects, the talk will focus on spin  $S = 1/2$  systems. In particular, application of chirp SIFTER for distance determination will be demonstrated. The sensitivity gain with respect to DEER is shown for different spin environments and orientation selection is discussed for a set of rather stiff polyphenylene-ethylene compounds. We determine conditions under which distance distributions are not influenced by background correction. For high-density lipoprotein (HDL) particles, chirp SIFTER allows determination of an interspin distance that is longer than the sensitivity limit of 4-pulse DEER. EPR measurements are compared to FRET with respect to orientation selection as well as the extracted distance.

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## ESR Spectroscopy of Structural Phase Transitions and Dynamic Effects in Hybrid Metal-Formate Perovskite Frameworks

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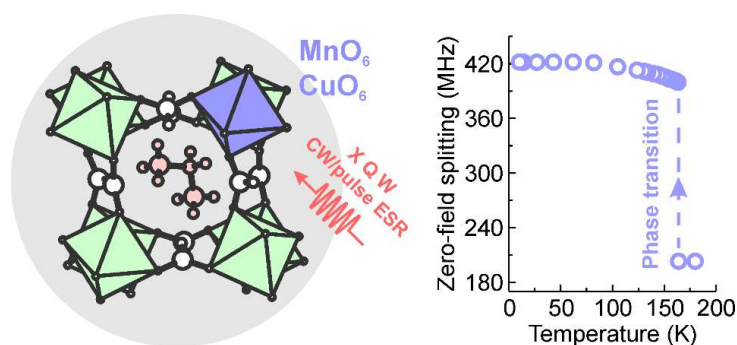
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Perovskite formate frameworks constitute an emerging family of hybrid materials with interesting dielectric, ferroelectric and magnetic properties.<sup>[1]</sup> These compounds are composed of metal centers joined together by formate linkers forming frameworks with cuboid nanocavities. Each such cavity confines a single molecular cation, which is H-bonded with the framework. The majority of these hybrid compounds exhibit structural phase transitions followed by the molecular cation ordering and framework deformation. Here we present a CW and pulse ESR study of structural phase transitions and dynamic effects in zinc-formate frameworks doped with small amount of paramagnetic transition metal ions. The temperature dependent multifrequency CW ESR spectra reveal molecular cation dynamics and type of the structural phase transitions (Figure 1).<sup>[2,3]</sup> CW ESR experiments with applied external electric field are employed to elucidate the ferroelectric nature of these compounds. Pulse ESR and ENDOR measurements are performed to study the structure of the frameworks, lattice dynamics and motion of the molecular cations in the ordered phases.<sup>[4]</sup>



**Figure 1.** Crystal structure and temperature dependence of the axial zero-field splitting parameter of  $\text{Mn}^{2+}$  doped  $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}(\text{HCOO})_3]$  framework.

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## Room-Temperature EPR Distance Measurements Using Trityl and Nitroxide Spin Labels

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Electron Paramagnetic Resonance (EPR) based nanometer distance measurements at ambient temperatures are of particular interest for structural biology applications.<sup>[1,2]</sup> The commonly used in EPR nitroxide spin labels reveal somewhat too short transverse relaxation at these conditions,<sup>[3]</sup> which limits their use for detecting static dipolar interactions. At the same time trityl radicals have long enough electron spin relaxation time,<sup>[4]</sup> and narrow EPR spectrum that allow applying single frequency EPR techniques at room temperature. Sometime it is easily to introduce orthogonal spin labels trityl/nitroxide. In these condition the still long enough longitudinal relaxation of nitroxide spin labels allows to use them as ‘pumped’ species in combination with detection on the slower relaxing Triarylmethyl (TAM) spin labels in the Relaxation Induced Dipolar Modulation Enhancement (RIDME) experiment. In the present work, we report first demonstration of room-temperature RIDME distance measurements in nucleic acids using TAM as slow-relaxing detected species and traditional nitroxide as fast-relaxing partner spin. Two types of immobilizers, glassy trehalose and modified silica gels Nucleosil, were used for immobilization of the spin labeled biomolecules. The room-temperature RIDME-based distance distributions are in good agreement with those measured at 80 K by other techniques. Room-temperature RIDME on spin pairs trityl/nitroxide may become a useful method for structural characterization of biomacromolecules and biomolecular complexes at near physiological temperatures.

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## 'End-to-End' Stacking of Small dsRNA Studied with PELDOR/DEER

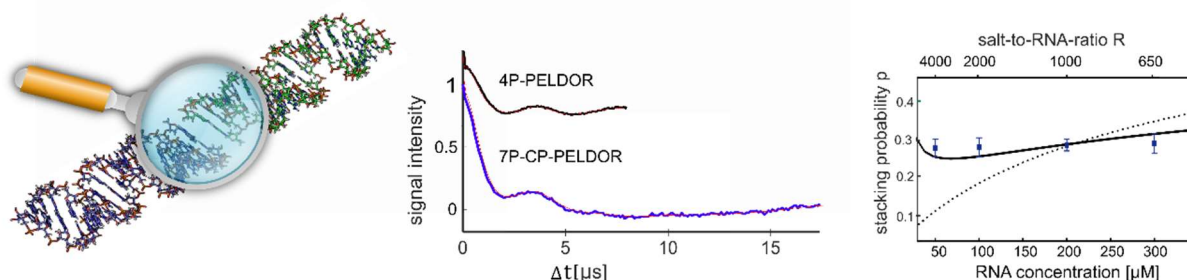
Nicole Erlenbach,<sup>1</sup> Christian Grünewald,<sup>2</sup> Bisera Krstic,<sup>1</sup> Alexander Heckel<sup>2</sup> and Thomas F. Prisner<sup>1</sup>

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PELDOR (pulse electron-electron double resonance)<sup>[1]</sup> is an established method to study intramolecular distances which can give evidence for conformational changes and flexibility. However, it can also be used to study intermolecular interaction as for example aggregation. One example for such a study is the 'end-to-end' stacking of small double-stranded (ds)RNAs. In the last decade, several groups have shown that small dsRNAs tend to form rod-like structure due to  $\pi$ - $\pi$ -interactions between the base pairs at the end of the strands.<sup>[2-4]</sup> As shown by Ryter and Schulz,<sup>[5]</sup> this can play an important role in RNA-protein interaction. However, it can also influence or complicate measurements like PELDOR when aiming for intramolecular geometry and dynamics.

To gain a deeper understanding on this interaction, 4-pulse<sup>[6]</sup> and 7-pulse (CP)<sup>[7]</sup> PELDOR was used on singly labelled (20mer) dsRNA. The resulting distances report on the stacking geometry of the RNA duplexes. The modulation depth of the PELDOR measurements can be used to determine the stacking probability. Measured as a function of salt and RNA concentration demonstrated that the stacking probability depends on the salt-to-RNA ratio.<sup>[8]</sup> Moreover, we could show that single base overhangs at both ends are able to impede this interaction.



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# Application of EPR Methodology Towards Cr/PNP Based Ethylene Tetramerisation Catalysis

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Ethylene oligomerisation is an industrially important route to linear  $\alpha$ -olefins (LAO), especially 1-hexene and 1-octene, co-monomers for polyethylene.<sup>[1,2]</sup> Increasing demand for these LAO has propelled research into selective trimerisation and tetramerisation. Commercialised ethylene tetramerisation catalysis involves highly active Cr/PNP (PNP =  $(R^2)_2PN(R^1)P(R^2)_2$ ) based catalyst systems leading to 70% selectivity for industrial 1-octene production. However, the active catalyst and detailed mechanism underlying this catalysis are still unclear.<sup>[1-3]</sup> The active catalyst is formed by adding an activator to the Cr<sup>I</sup> or Cr<sup>III</sup> precursor in presence of a PNP ligand and a salt of a weakly coordinating anion such as  $(Al(OC(CF_3)_3)_4)^-$  to start the reaction. The complex can undergo ligand redistributions, reduction and disproportionation, resulting in the formation of various species with different oxidation states and as a result altered total electron spin.

Paramagnetic species from discrete catalyst precursors to ongoing catalysis were examined *in situ* by continuous wave electron paramagnetic resonance (cw-EPR) spectroscopy. In the context of catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. To this end, relaxation filter based pulse EPR methods were employed on a mixture of discrete Cr<sup>I</sup> and Cr<sup>III</sup> precursors with different spin states to demonstrate recovery of their individual spectra.<sup>[4]</sup> The use of this method on an activated Cr precatalyst will be illustrated for monitoring the various species. To obtain additional structural information to these intermediates pulse EPR methods such as transient nutation experiments for assessing their spin states and hyperfine spectroscopy methods for measuring small couplings that were unresolved in CW spectra in combination with a quantum chemistry approach have been applied. The use of these methods for assessment of observed intermediates and their relevance to the catalysis under different catalytic conditions will be presented. The full armory of EPR techniques applied to an activated catalyst mixture provides the first unequivocal evidence for a bis-ethylene Cr<sup>I</sup> species that has previously been a proposed intermediate in the industrial process but has so far been elusive.

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## Gadolinium and Nitroxide Labels to Measure Protein Interactions at Room Temperature with High Field CW EPR and ODNP

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The protein Bim inhibits the anti-apoptotic protein Bcl-xL and activates the apoptotic effector protein Bax, which marks the point of no return in the mitochondrial pathway of apoptosis.<sup>[1,2]</sup> For Bax activation and Bcl-xL inhibition, only the BH3-domain of Bim is required, which we synthesized and spin labeled with nitroxide and gadolinium probes. We characterized a 16 and 26 amino acid Bim BH3-peptide with DEER at cryogenic temperatures and showed that, depending on the peptide length, dimers are formed in aqueous solution, and can be dissolved by addition of organic solvents or interacting protein partners (Bcl-xL). Orthogonal labels were employed to distinguish peptide-peptide from peptide-protein interactions via DEER.

Here we show that it is possible to use Gd labels to qualitatively monitor the inter-peptide and peptide-protein interactions using a novel high field (240 GHz)<sup>[3]</sup> room temperature cw EPR technique. Peptide binding to Bcl-xL could also be detected at room temperature following changes in the water hydration of nitroxide-labeled peptides via ODNP.<sup>[4]</sup> By transient recording of room temperature cw EPR we detected the activity of orthogonally-labeled peptides using the nitroxide labels as reporter groups of side chain dynamics, and the Gd labels eventually present in the sample as silent spectators. These novel room temperature EPR tools open a new perspective to study protein interactions under physiological conditions.

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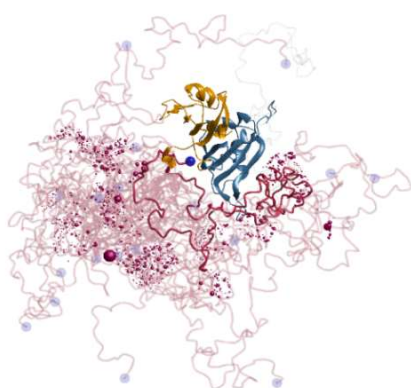
## Disordered Protein Domains and Distance Measurements by Pulsed EPR - A Match Made in Heaven?

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Distance measurements obtained with a combination of site-directed spin labelling (SDSL) and pulsed dipolar spectroscopy (PDS) have become an important source of structural information in biological systems.<sup>[1,2]</sup> The power of this approach is, among other factors, related to the high sensitivity, which enables measurements in the low micromolar spin concentration range. Furthermore, analysis of PDS data results in distance distributions that represent the conformational heterogeneity of the biomolecule of interest and thus indirectly characterize the space explored by dynamics of the system. Such information is very valuable for protein domains that do not adopt a stable fold in solution, typically known as intrinsically disordered domains (IDDs).



**Figure 1.** NMR structure of the RNA recognition motifs of hnRNPA1 (blue and orange) and ensemble model of the disordered C-terminal domain (red) with simulated spin label positions (spheres); pdb: 2LYV<sup>[6]</sup>

By definition, IDDs feature large conformational flexibility, and they are often highly aggregation prone, enforcing low sample concentrations. Their ability to adopt a multitude of conformations also reflects in a diverse phase diagram of accessible (multimeric) states, for example liquid-liquid phase separation (LLPS) has been observed.<sup>[3]</sup> We performed SDSL of the human splicing regulator hnRNPA1,<sup>[3,4]</sup> which contains a large IDD (~120 amino acids). Using distance restraints predominantly measured between residues in the IDD and sites in the structured domains of the protein enabled us to generate the first experimentally restrained ensemble model of the full-length protein chain.<sup>[5]</sup> Independent paramagnetic relaxation enhancement measurements were performed to validate the structural ensemble model. Spin dilution experiments in combination with orthogonal spin labelling were used to compare conformations, and to monitor protein interactions in the dispersed and the LLPS state.

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## Radical States Involved in the Charge Separation Process and in the Photodegradation of Fullerene-Free Organic Solar Cell Materials

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The bulk heterojunction (BHJ) organic solar cell (OSC) holds promise for low-cost and versatile solar energy collection. The BHJ layer consists of intermixed regions of molecules with electron donor and acceptor properties, D and A, respectively, allowing for efficient charge separation at the interface between the materials (see Figure). While fullerene derivatives have for two decades been near-unavoidable as acceptors, this has recently changed with the advent of efficient nonfullerene acceptors (NFAs) leading to fullerene-free devices with by now record power conversion efficiencies (PCE) among BHJ OSCs.<sup>[1]</sup> Examples will be discussed in which the EPR toolbox was used to investigate novel blends with NFAs in pristine state as well as after photodegradation.

In BHJ OSCs, charge separation at the D/A interface leads to positive and negative charge carriers, called P<sup>+</sup> and P<sup>-</sup> polarons, in the D and A region, respectively, which are organic radicals with often overlapping EPR spectra even at higher microwave frequencies. In a state-of-the-art fullerene-free D/A blend, two methods have been demonstrated to disentangle the respective spectra using pulse EPR spectroscopy in W-band: (i) Relaxation-filtered EPR based on the difference in spin population relaxation times T<sub>1</sub> of the two radicals, and (ii) Electron-electron double resonance (ELDOR)-detected NMR (EDNMR) exploiting for selective detection the presence of nitrogen nuclei in only one of the molecules.<sup>[2]</sup> The separate spectra of the polarons provide accurate EPR parameters for comparison with DFT calculations, as demonstrated in several D/A blends.

Besides the advantageous charge separation, there are detrimental processes occurring under illumination in the presence of oxygen, causing materials degradation and limiting the OSC lifespan. Light-induced EPR for radical detection, optically detected magnetic resonance (ODMR) for monitoring of triplet exciton production, and spin-trap experiments to evaluate the generation of radical oxygen species were combined with optical spectroscopy to obtain a detailed picture of the photodegradation process.<sup>[3]</sup> In blends of a donor polymer and a small molecule NFA, the charge separation is shown to compete with TE production, effectively tempering the production of singlet oxygen and thus the related degradation of the NFA.

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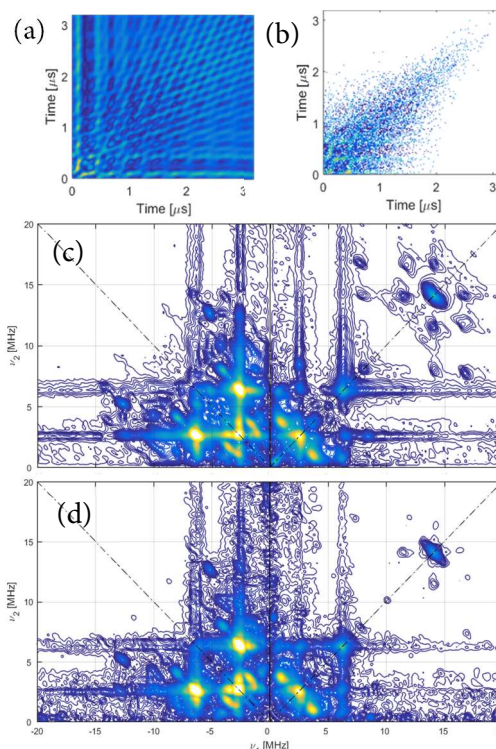
# Hyscorean: Measurement, Processing and Analysis of Non-Uniform Sampled HYSCORE

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In conventional uniformly sampled methods, the potential resolution and sensitivity gain are limited by the time required to complete the experiments. Due to constrained available measurements times, spectroscopists tend to find a balance between digital resolution and signal-to-noise ratio to match the available time resulting in potentially sub-optimal data. Non-uniform sampling (NUS) opens the possibility to sample a subset of the original data in order to potentially improve spectral resolution and sensitivity while reducing the measurement times. NUS was assessed for HYSCORE spectroscopy by *in silico* tests.<sup>[1]</sup> However, due to technical limitations of commercial spectrometers NUS has not been realized experimentally to date in EPR experiments. Exploiting the limited flexibility offered by the PulseSPEL and ProDeL environments a program has been developed for NUS measurements on commercial Bruker spectrometers controlled by the XEPR software.

Data acquired this way requires further processing steps in comparison to uniformly sampled data. To facilitate this additional processing, we present Hyscorean (HYSCORE ANalysis): a new free software package for the MATLAB environment, which includes all necessary files for setting up such measurements as well as a GUI-based program which enables the reconstruction and processing of uniform and non-uniform sampled HYSCORE data. The software includes state-of-the-art reconstruction algorithms, a validation module to estimate the uncertainty introduced by the NUS, and a new fitting module powered by EasySpin. As a proof of concept, NUS HYSCORE spectra of an iron myoglobin-variant<sup>[2]</sup> have been measured with sampling only 15% of the total points and compared to uniform sampling (Figure 1). The spectra were acquired on a commercial Bruker spectrometer in reduced time, processed with Hyscorean and are analysed in terms of their reconstruction parameters.



**Figure 1.** HYSCORE spectrum of an iron myoglobin variant sampled (a,c) uniformly (100% sampling) and (b,d) non-uniformly (15% sampling) on a commercial Bruker spectrometer.

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## Direct Prediction of EPR Spectra from MD Simulations of Lipid Bilayers – a Route to Understanding Structure and Dynamics in Biological Membranes

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We report the first prediction of variable temperature EPR spectra of model lipid bilayers in the presence and absence of cholesterol from the results of large scale fully atomistic Molecular Dynamics (MD) simulations.<sup>[1]</sup> Three types of structurally different nitroxide spin probes were employed in order to study different parts of the bilayer composed of dipal-mitoylphosphatidylcholine (DPPC) lipids. EPR spectra are predicted directly from long MD trajectories using our MD-EPR simulation methodology.<sup>[2–4]</sup> The results demonstrate very good agreement with experiment confirming the accuracy of the latest lipid force fields (Slipids).

The atomic resolution of the simulations allows the interpretation of the molecular motions and interactions in terms of their impact on the sensitive EPR line shapes. Effects of cholesterol on the dynamics and order of spin probes are analysed and correlated with the stabilising/destabilising effects of cholesterol on the host lipids.

Given the complexity of structural organisation in lipid bilayers the advantage of using the combined MD-EPR simulation approach is two-fold. Firstly, prediction of EPR line shapes directly from MD trajectories of actual phospholipid structures allows unambiguous interpretation of EPR spectra of biological membranes in terms of complex multi-component motions, avoiding the uncertainty arising from the fitting of spectra employed in previous studies. Secondly, such a synergistic MD-EPR approach provides an ultimate test bed for the up-to-date MD simulation models employed in the studies of biological membranes, an area that currently attracts great attention.

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# Analysis of the EPR Spectra of Transferrin: The Importance of Zero-Field-Splitting Distributions and 4th-Order Terms

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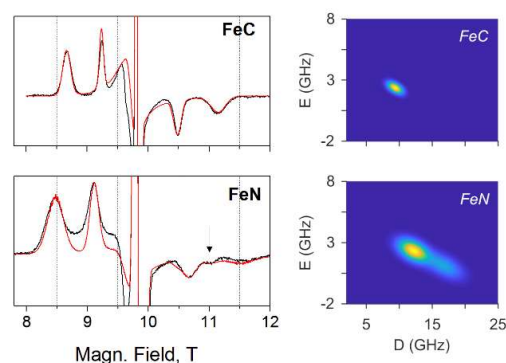
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In 1960, Castner *et al.* reported an X-band EPR study of iron ions in glass.<sup>[1]</sup> They observed “a broad smear extending from  $g \cong 10$  at low fields to above  $g = 1$  at high fields, with an intense and sharp resonance at  $g = 4.27$ .” They, correctly, assigned the  $g = 4.27$  resonance to transitions within the  $|\pm^{3/2}\rangle$ -doublet of high-spin  $\text{Fe}^{3+}$  ( $S = 5/2$ ). However, a quantitative analysis of the spectrum in terms of spin-Hamiltonian parameters as well as a structural interpretation of the smear are still lacking today. This is unfortunate, since proteins and enzymes with high-spin  $\text{Fe}^{3+}$  in their active site show similar spectra and EPR spectroscopy could be most helpful to elucidate structure-function relations and operating mechanisms.

The zero-field-splitting (ZFS) parameters of a high-spin  $\text{Fe}^{3+}$  site are a sensitive probe of its structure. Broad distributions in the ZFS parameters reflect conformational heterogeneity in the frozen solution, but complicate analysis of the spectra. Recently we developed a numerical procedure, termed the grid-of-errors, to extract the distribution of ZFS parameters from high-frequency EPR spectra without making any assumption on its physical origin.<sup>[2]</sup>

Here we apply the grid-of-errors to characterize the iron-binding sites of transferrin, a protein of which we earlier reported high-quality EPR spectra at 275 GHz.<sup>[3]</sup> The procedure leads to improved spectral simulations and we find that the ZFS distributions are as characteristic of an iron site as the ZFS parameters themselves (Figure 1). However, a ZFS distribution cannot account for a double peak in the X-band spectrum near  $g = 4.27$ , the enigmatic fingerprint of transferrin. Instead, we show that the double peak stems from the term  $B_4^{-3}O_4^{-3}(S)$  in the spin Hamiltonian. Our approach is generally applicable to high-spin  $\text{Fe}^{3+}$  systems and an important step towards exploiting the full potential of multi-frequency EPR to investigate iron in proteins and enzymes.



**Figure 1.** Left: 275.7 GHz EPR spectra of human serum transferrin C-lobe (FeC) and N-lobe (FeN), black: experiment; red: simulation. Right: Contour plots of the ZFS distributions.

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## The Tale of the Cellular Copper Cycle

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Copper's ability to accept and donate single electrons makes it an ideal redox cofactor, and thus one of the most essential metal ions to the survival of the cell. However, copper ions are also involved in the Fenton reaction and hence capable of driving the generation of deleterious hydroxyl radicals, which are deleterious to the cell. Hence, both prokaryotic and eukaryotic systems have developed a considerable regulation mechanism to maintain negligible copper concentration, in the femtomolar concentration.

Deciphering this regulation mechanism in eukaryotic and prokaryotic systems is tremendously important from several reasons: first, it will assist in developing new therapeutic agents that will control the in-cell copper concentration. Second, copper has been used throughout much of the human civilization as an antimicrobial agent, and understanding its cellular pathway can lead to development of new generation of antibiotics. In this talk, I will shed light on several important copper regulation systems in the human cell and in E.coli: the human Ctr1-Atox1-ATP7b pathway,<sup>[1-4]</sup> the copper periplasmic efflux system, CusCFBA,<sup>[5,6]</sup> and the Cu(I) metal sensor, gene expression regulation system, CueR.<sup>[7,8]</sup> Using Electron Paramagnetic Resonance (EPR) spectroscopy, along with biochemical and computational work, I will present structural models for Ctr1-Atox1-ATP7B system, CusB and CueR in the apo and functional state.<sup>[1,2,4,6,9-12]</sup> Then, based on the structural constraints and cell data I will explain their mechanism of action. Last, I will demonstrate how basic understanding of the function of these systems can assist us in designing new class of biomarkers and antibiotics.

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## Electric Field Modulation of Magnetic Exchange in Molecular Helices

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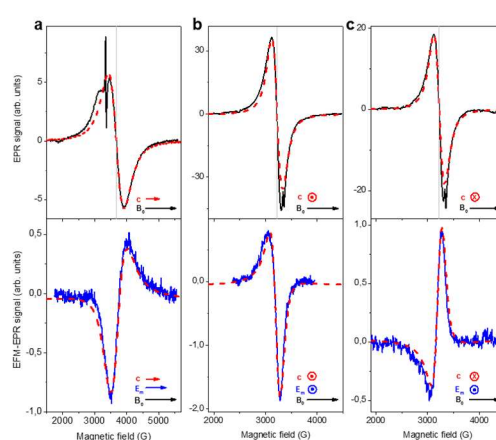
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The possibility to operate on magnetic materials through the application of electric rather than magnetic fields - thus with faster, less energy demanding, and more space-confined control - makes the investigation of magnetoelectric effects one of the most active research field in material science.<sup>[1]</sup> An unprecedented magneto-electric phenomenon was recently predicted in metal-radical helices.<sup>[2]</sup> On one of these systems (a Mn-radical helix), the application of an electric field ( $E$ ) introduces an energy contribution, which is different in case of parallel or antiparallel alignment of the spins along the helix. In other words, the  $E$  field modulates the intra-chain exchange interaction  $J$ . Even if this modulation is small, its effect is here reported as observed by exploiting the sensitivity of EPR in combination with a modulation of the  $E$  field.<sup>[3]</sup> It is in fact well known that one-dimensional spin correlation can induce a significant  $g$ -shift even when only a weak anisotropy of dipolar origin is present.<sup>[4]</sup> By modulating the  $E$  field in the EPR experiment a modulation of  $J$  is induced, which is reflected in the modulation of the resonance frequency, in absence of the usual magnetic field modulation. The symmetry of the observed phenomenon unambiguously confirms its magneto-chiral nature.



**Figure 1.** EPR spectra (top panel, black lines) and Electric Field Modulated (EFM) -EPR spectra (bottom panel, blue lines) acquired at 30 K in different configurations. Corresponding simulations red lines.

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## Host-guest Interactions in Polysaccharide Hydrogels Evidenced by Spin Probes

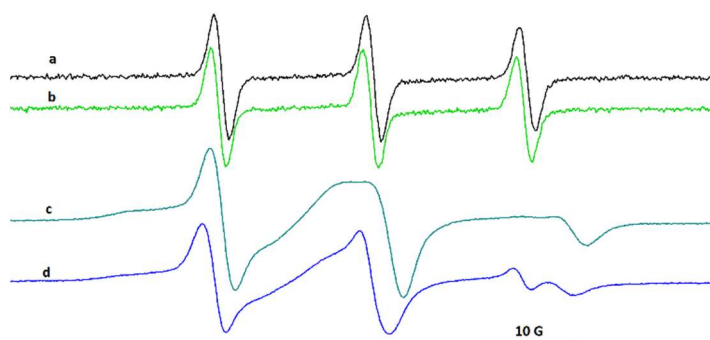
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Polysaccharide hydrogels are a class of materials with wide biomedical applications including contact lenses, wound dressings and delivery carriers for bioactive substances, due to their high degree of biocompatibility. Alginate is a type of polysaccharide gelator that generates hydrogels in the presence of different divalent cations.<sup>[1]</sup> In this work, the alginate chains were functionalised with  $\beta$ -cyclodextrin ( $\beta$ -CD) and adamantane. The new hydrogels were characterised by rheological measurements which evidenced

that alginate functionalisation with  $\beta$ -CD through short alkyl linkers and with adamantane influences the mechanical properties of the hydrogels. The resulting hydrogels are softer compared to non-modified alginate, as the rheological parameters have decreased values. In the mixture of adamantane functionalised alginate and  $\beta$ -CD functionalised alginate, host-guest interactions occur and this leads to the lowest ability of metal ions to complex alginate.

In many cases, the macroscopic (global) changes in inhomogeneous materials like gels can be correlated with local changes successfully evidenced by EPR measurements.<sup>[2]</sup> The host-guest interactions in  $\beta$ -CD functionalised alginate are easily evidenced by spin labelling of the polysaccharide or by using spin probes. For instance, we monitored the diffusion of dual molecular probes bearing dansyl and TEMPO moieties linked by heptane-1,7-diamine ( $DA_{1,7}T$ ) in alginate gels. In Figure 1 are shown the EPR spectra in different alginate gels evidencing different features that are correlated with alginate functionalisation. These changes will be discussed in the presentation.



**Figure 1.** EPR spectra of  $DA_{1,7}T$  in: a) alginate gel, b) adamantane-functionalised alginate gel, c)  $\beta$ -CD-functionalised alginate gel, d) adamantane and  $\beta$ -CD functionalised gel.

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## Gd(III)-Gd(III) RIDME for In-Cell EPR Distance Determination

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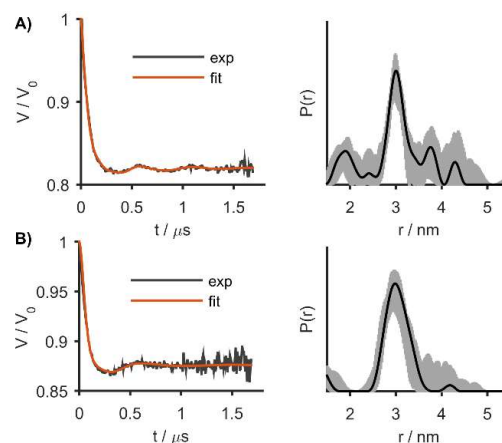
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In-cell distance determination by EPR reveals essential structural information about biomacromolecules under native conditions. We demonstrate that the pulsed EPR technique RIDME (relaxation induced dipolar modulation enhancement) can be utilized for such distance measurements.

In vitro RIDME measurements between Gd(III)-based spin labels have no bandwidth limitations, as compared to conventional DEER (double electron-electron resonance). As a consequence, the effects of pseudo-secular terms become negligibly small and the modulation depth is increased. Indeed, the modulation depth of 50% was measured for Gd(III)-Gd(III) RIDME in a deuterated solution, which is 10 times higher than in a similar DEER measurement.<sup>[1]</sup>

In-cell RIDME implies that the measurement is performed in protonated media, where relaxation is faster and spin diffusion is stronger. This makes the signal decay in RIDME very fast and acquisition of the dipolar evolution challenging. Carefully chosen experimental conditions allow to acquire a RIDME time trace of at least 2  $\mu$ s for molecular rulers that bear Gd-PyMTA spin labels. The sets of overtone coefficients are different for protonated and deuterated solutions. The analysis of in-extract and in-cell RIDME data, obtained for *X. laevis* oocytes, shows that the overtone coefficients can be taken the same as for protonated solutions. The distance distributions measured in the cellular environment are in perfect agreement with expectations. Owing to an increased modulation depth and the absence of artefacts at short distances, Gd(III)-Gd(III) RIDME has a potential to become a method of choice for in-cell distance determination.



**Figure 1.** The RIDME form factors (left) and the corresponding distance distributions (right) for Gd-ruler-3.0 in cell extract (A) and in oocytes (B).

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## Electron-Nuclear Polarization Transfer in ENDOR and Liquid DNP to Study Biomolecules

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Electron-nuclear double resonance (ENDOR) and dynamic nuclear polarization (DNP) are two techniques based on polarization transfer between electron and nuclear spins. Despite differences in the experimental realization, their similarities rely on the detailed mechanism of hyperfine interactions and their time scales. The lecture will give an overview of our recent developments in these two methods in solids (ENDOR) and solution (Overhauser DNP) to study biological systems. To this end, design and implementation of coupled EPR/NMR experiments at various microwave frequencies, particularly in the high-frequency/high-field EPR regime, has been in focus. Taking advantage of dynamic nuclear polarization in the liquid state at room temperature, we could recently generate  $^{13}\text{C}$  NMR signal enhancements on small molecules up to three orders of magnitude. Our most representative application for high-frequency EPR/ENDOR methods has been the study of enzymatic reactions involving paramagnetic intermediates, particularly the unprecedented long-range proton-coupled electron transfer (PCET) in *E. coli* ribonucleotide reductase (RNR). Using a combination of high-field EPR and ENDOR (94 and 263 GHz) with quantum chemical calculations, we could determine the hydrogen bond network around three essential tyrosyl radical intermediates.

## Light-Induced Pulsed EPR Dipolar Spectroscopy: The Triplet State Probe

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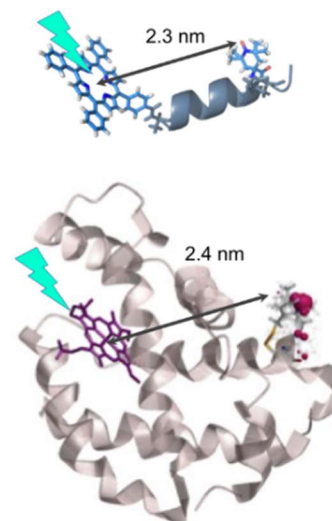
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Light-induced pulsed EPR dipolar spectroscopy (PDS) allows the determination of nanometer distances between paramagnetic sites, employing as orthogonal spin labels a chromophore triplet state and a stable radical.<sup>[1,2]</sup> The distinctive properties of the triplet state, *in primis* the spin polarization enhancement of the EPR signal and the photoinduced behavior of the spin probe, have been successfully exploited.

The versatility of this methodology is ensured by the employment of different techniques: in addition to double electron electron resonance (DEER/PELDOR), relaxation-induced dipolar modulation enhancement (RIDME) is applied for the first time to the photoexcited triplet state. An alternative pulse scheme for laser-induced magnetic dipole (LaserIMD) spectroscopy, based on the refocused-echo detection sequence, is proposed for accurate zero-time determination and reliable distance analysis.<sup>[3]</sup> These techniques complement each other and, depending on the nature of the triplet spin label, they can be used interchangeably to take advantage of specific characteristics, selecting the pulse sequence that yields the best performance for the system of interest. Light-induced PDS has been applied on a peptide-based spectroscopic ruler<sup>[2]</sup> in order to test the accuracy, sensitivity and distance limits and extended to paradigmatic proteins in order to prove the feasibility of distance measurements using endogenous triplet state probes found in different classes of proteins.<sup>[3,4]</sup>

A computational study of the triplet state performance, based on the density matrix formalism, has allowed the effects of both the electron spin polarization and zero-field parameters on the dipolar traces to be understood. Benchmark systems, covering the range of spectroscopic parameters encountered in chromophores used in EPR spectroscopy, have been investigated proving that the triplet state is a reliable probe for distance analysis.



**Figure 1.** Peptide-based model system containing a porphyrin chromophore and TOAC nitroxide and a protein containing an endogenous porphyrin and singly labelled with MTSSL.

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## Twist-Angle Dependence of Triplet State Properties in Twisted Acenes

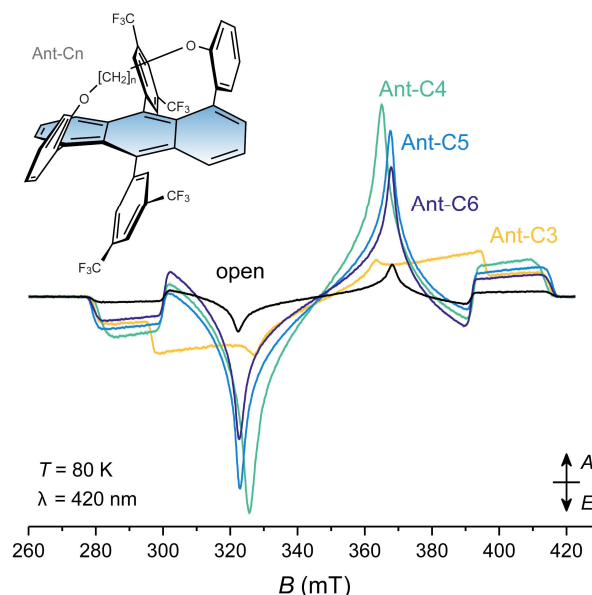
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Acenes are a fundamental building block of many compounds showing promise in the field of organic electronics, as their electronic, optical and magnetic properties can be modulated by changes in the chemical structure.<sup>[1]</sup> In addition to changes in the number of annulated rings and in the nature of the substituents, varying degrees of deviations from planarity of the  $\pi$ -system of the acene core can also be introduced, providing ample opportunity for fine-tuning of the molecular properties. Recently, a series of tethered twisted acenes has been synthesised, in which the twist angle is solely determined by the length of the tether, thus separating the effect of substituents from that of the twist angle and providing an ideal series of compounds for the investigation of the twist-angle-dependence of the electronic and magnetic properties.<sup>[2]</sup> In this study, we investigated the photoexcited triplet states of a series of twisted acenes based on an anthracene core by transient and pulse EPR. The triplet yield was found to increase with increasing twist angle, in agreement with the results from previous optical studies,<sup>[2]</sup> confirming an increased ISC probability for the twisted compounds compared to the untethered parent compound. Transient EPR measurements of the twisted acenes in frozen solution revealed changes in zero-field splitting, showing a trend towards decreasing  $D$  with increasing twist angle and a clear increase in the rhombicity of the ZFS tensor. The spin polarisation of the transient EPR spectra was also found to change with increasing twist angle, indicating changes in the sublevel population kinetics depending on the deviation of the  $\pi$ -system from planarity.

ENDOR measurements were performed to better characterise the triplet state wavefunctions. The presence of only small shifts in the positions of the proton ENDOR peaks recorded for the canonical orientations indicate a minor influence of the twist angle on the extent of the triplet spin density distribution. In addition to the dependence on twist angle, an excitation wavelength dependence of both the transient EPR and the ENDOR spectra was observed, suggesting the presence in solution of molecules with a range of different twist angles.



**Figure 1.** Transient EPR spectra of twisted acenes with three to six carbon atoms in the linker.

[1] J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028.

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## ELDOR-detected NMR: The Curious Case of a Coupled Copper Complex

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ELDOR-detected NMR (EDNMR) is a pulsed EPR technique usually applied to measure hyperfine and nuclear quadrupole couplings. It makes use of a high turning angle (HTA)  $\mu\text{w}$ -pulse that drives formally forbidden electron-nuclear transitions which creates side holes, offset by the nuclear frequencies. A spectrum is obtained by sweeping the frequency of the ELDOR source while keeping the observer frequency constant.<sup>[1]</sup>

We will present experimental data and simulations which show that EDNMR spectra also contain information about moderately sized electron-electron couplings.<sup>[2]</sup> In the case of a fused Cu(II)-porphyrin dimer with large exchange coupling (80 GHz), Q-band EDNMR spectra show signal enhancements that encode a zero-field splitting of 240 MHz. This is about twice as large as expected from a simple point-dipole approximation ( $r = 8.4 \text{ \AA}$ ).

Simulations were performed with an algorithm by Cox *et al.*,<sup>[3]</sup> which we generalized such that it is now possible to treat systems with arbitrary electron spins and arbitrary magnitude of the different interactions. In the case of a *meso-meso* linked Cu(II)-porphyrin dimer with a perpendicular arrangement of the porphyrin moieties, the Q-band EDNMR spectra can be simulated by assuming isolated copper sites. The resolution is high enough to resolve  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  peaks as well as the metal ion nuclear quadrupole coupling in glassy frozen solution.

The systems investigated here are interesting because they are suitable building blocks for molecular wires. However, our findings suggest that EDNMR might more generally be a method of choice to investigate paramagnetic multi-nuclear metal complexes.

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## 'To Each His Own': Spin-Labeled Nanobodies as Proteins' Conformational Reporters

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Nanobodies (*i.e.* single-domain antibodies) are promising new tools for in-cell applications due to their low molecular weight, their protein- and state-specificity, nano- or sub-nano-molar affinity to their target and the possibility to be inserted into cells. We propose here the use of spin-labeled nanobodies as conformational reporters of wild type unlabeled proteins via DEER spectroscopy.

We focused on a set of spin-labeled nanobodies targeting ABC transporters, proteins that couple the energy deriving from the binding and hydrolysis of ATP to large-amplitude motions that enable substrate translocation across membranes. These molecular machines have been studied in different environments (such as detergent, liposomes and nanodiscs) via EPR, X-ray crystallography, cryo-EM and fluorescence techniques. In this framework, the challenge ahead is the investigation of their conformational plasticity in a native environment.

We show the applicability of gadolinium- and nitroxide-labeled nanobodies for two different systems previously investigated in our lab:<sup>[1,2]</sup> the homodimeric exporter MsbA and the heterodimeric TM287/288. In the first case, a non-state specific natural nanobody with picomolar affinity has been used to monitor the inward- to outward-facing transition of the unlabeled transporter. In the second case a “cocktail” of state- and non-state specific nanobodies binding to different sites of the protein could be used to obtain a fingerprint distance of the outward-facing state of the transporter. Orthogonal labels attached to the transporters were also used to corroborate and strengthen the findings. The sensitivity of the high-power AWG Q-band spectrometer allowed to obtain reliable structural information at low micromolar protein concentrations, which are close to the physiological conditions, paving the way for the use of biocompatible Gd-labelled nanobodies in cells.

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## Imaging Free Radicals Using Field-Cycling Overhauser-Effect MRI

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Over several decades significant effort has been devoted to imaging the distribution of free radicals in biological systems, including *in vivo* studies. While “direct” EPR imaging (EPRI) (CW or pulsed) is possible, it may suffer from relatively poor resolution, long acquisition times and lack of anatomical reference images. An alternative method uses the Overhauser effect in combination with Magnetic Resonance Imaging (MRI), in a method known as Proton-Electron Double-Resonance Imaging (PEDRI) or, equivalently, as Overhauser MRI (OMRI).<sup>[1,2]</sup> The sample’s EPR is irradiated during the acquisition of a proton NMR image; parts of the sample containing unpaired electrons exhibit altered image intensity due to the Overhauser transfer of polarisation from electron to proton spins, revealing the location of the free radical.

Low magnetic fields are usually employed in order to achieve adequate penetration of the EPR irradiation and to avoid overheating the sample through non-resonant absorption; for example, *in vivo* PEDRI studies have been performed on rats at 10 mT<sup>[3]</sup> and on mice at 20 mT.<sup>[4]</sup> The disadvantage of low fields is the inherently low signal-to-noise ratio (SNR). Fortunately, magnetic field-cycling can be employed to improve SNR. In Field-Cycled PEDRI (FC-PEDRI) the magnetic field is switched between a low value (the evolution field,  $B_0^E$ ) and a high value (the detection field,  $B_0^D$ ) during the pulse sequence.<sup>[5]</sup> EPR irradiation takes place at  $B_0^E$  (~4 mT) at low frequency (~100 MHz) and lasts for *ca.*  $3 \times T_1 \approx 500$  ms. The field is then switched to  $B_0^D$  and the NMR detection pulse(s) and magnetic field gradients for imaging are applied.

In our laboratory we have constructed two FC-PEDRI systems, both of which employed dual, coaxial magnets. In the first system a 60-cm bore permanent magnet provided a vertically-oriented detection field of 59 mT.<sup>[6]</sup> An internal, resistive, field-offset coil allowed the value of  $B_0^E$  could be selected. The second system used a 450 mT superconducting primary magnet, with a coaxial resistive, actively-shielded field-offset coil (12 cm bore).<sup>[7]</sup> Utsumi *et al.* have demonstrated an alternative approach using rotation of the sample low-field (20 mT) and high-field (1.5 T) regions for EPR irradiation and signal detection, respectively.

Applications of Overhauser techniques to date have included the study of exogenous free radicals as contrast agents, the use of probes of pH and for monitoring redox status or tissue oxygen concentration. Overhauser methods offer good spatial resolution and rapid acquisition, with spatially-registered anatomical proton MR images “for free”.

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## Mechanical Activation of an Ion Channel Triggered by Modification of Pressure Sensitive Nano-Pockets; a PELDOR, ESEEM and CW-EPR Study

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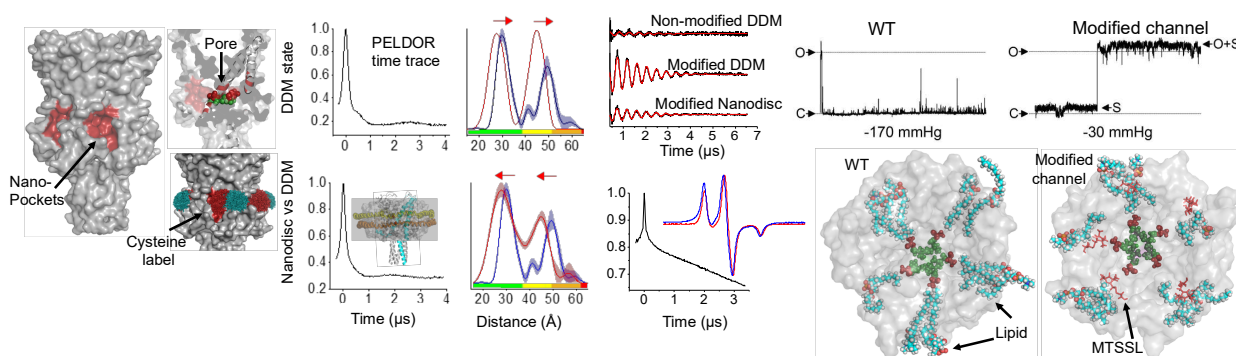
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Lipid availability within transmembrane nano-pockets (NPs) of ion channels has been linked with mechanosensitivity and it is known as the “lipid moves first” hypothesis. However, the effect of hindering lipid chain penetration into NPs on channel structure and function has not been demonstrated yet. Here we identify NPs on the large conductance mechanosensitive channel MscL (Figure 1), the ion channel with the highest pressure activation threshold in nature. We restrict lipid chain access to MscL’s NPs by cysteine modification and employ PELDOR/DEER spectroscopy with Site Directed Spin Labelling to interrogate channel conformation.

For a single site located at the entrance of the NPs and distal to the channel pore we generate an allosteric structural response in the absence of external applied pressure (Figure 1). Atomistic molecular dynamic simulations of the spin labeled channel embedded within lipid bilayers, demonstrate that specific label conformers restrict lipid chain access to the NPs (Figure 1).

Single channel recordings on this modified channel reveal a dramatic decrease in pressure activation threshold compared to WT and a novel sub-conducting state at null applied tension (Figure 1). Addition of a reducing agent and thus removal of the modification, reversed MscL’s pressure activation threshold back to WT channel levels. The modification associated with the conformational change restricted lipid access to the NPs, and thus interrupted the contact between the lipid and the NP mimicking the effect of bilayer tension. This method could be used to reversibly generate allosteric responses in mechanically gated channels.



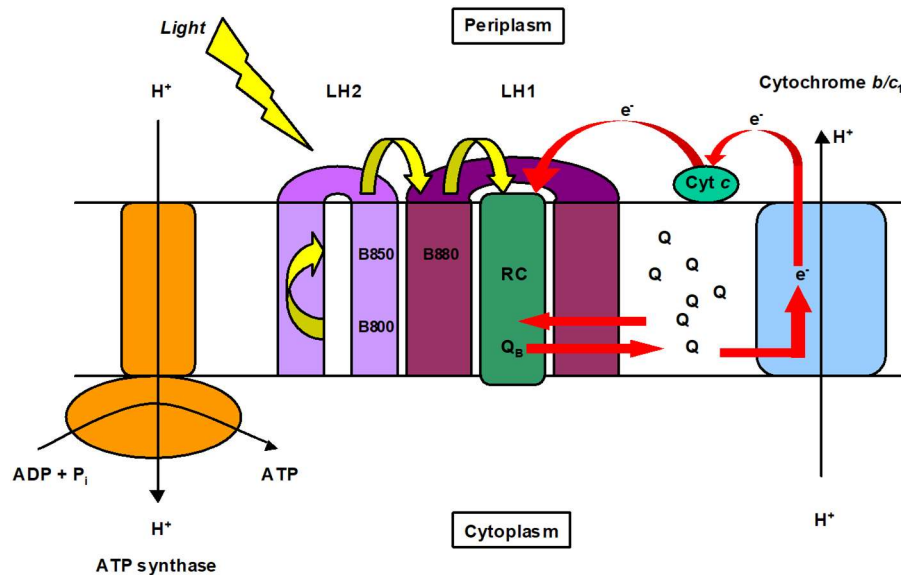
**Figure 1.** TbMscL NPs, pore constriction site & NP entrance labelling (left). PELDOR and ESEEM comparison e.g. DDM & Nanodiscs (middle). Example of PELDOR and CW-EPR (dipolar broadening) spectra of a mutation site with short distances. Single molecule recordings of WT & spin labelled MscL in presence of pressure. MD simulation of WT & spin labelled MscL in lipids.



## How Purple Photosynthetic Bacteria Harvest Solar Energy

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This picture shows a cartoon of the light reactions that take place in the membranes of a typical purple photosynthetic bacterium.<sup>[1,2]</sup> This presentation will describe the structure and function of the LH2 and LH1/RC pigment-protein complexes and how they cooperate to channel excitation energy to the RC (reaction centre) where that energy is trapped in a series of transmembrane redox reactions. The time taken for each energy transfer step in this pathway has been measured in real time and this will be reported.

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## A Tasting Menu of Dipolar Spectroscopies

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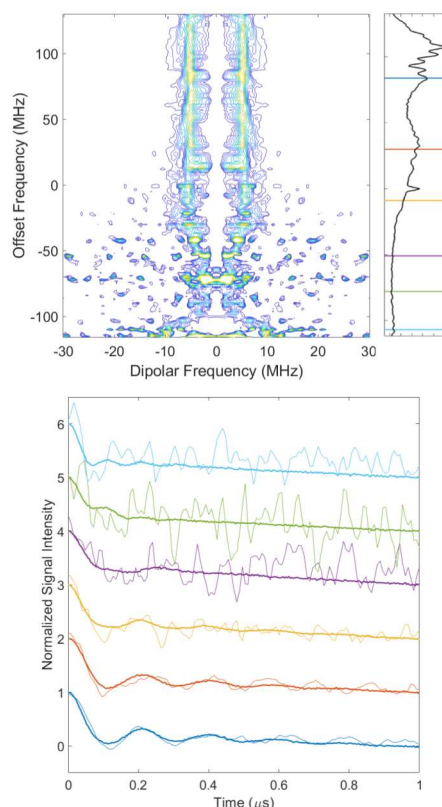
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Pulsed Dipolar Spectroscopy (PDS) is an important family of Electron Spin Resonance (ESR) techniques used to measure distance and orientation information on a length scale of ca. 1.5 - >10 nm.<sup>[1-3]</sup> Recent developments in this field have involved the use of shaped pulses formed using Arbitrary Waveform Generators (AWGs) and typically being either hyperbolic or CHIRP in nature. Combined with single frequency techniques, these have full resolution of orientation effects in a single experiment from frequency correlated spectra.<sup>[4,5]</sup> Another development in PDS has been the implementation of light-induced techniques; Light induced DEER (LiDEER) and Laser-Induced Magnetic Dipole spectroscopy (LaserIMD).

I will present a range of current projects involving different PDS methods. We show that it is possible to combine the single frequency LaserIMD with hyperbolic pulses to form a 2-dimensional experiment to probe the orientational contributions to the dipolar interaction in a model peptide system (Figure 1). We have also studied the orientation dependent interactions in a family of metal-containing porphyrin nano-rings using Double Electron-Electron Resonance (DEER) and Relaxation Induced Dipolar Modulation Enhancement (RIDME). Modelling of these datasets has allowed the relative signs and magnitudes of the dipolar and exchange coupling within these systems to be examined.

RIDME has previously been shown to be particularly useful for samples containing metal centres with broad spectra, a result of the absence of a bandwidth in the spontaneous spin inversion caused by  $T_1$ . However, the uncertainty in fitting and removing the unmodulated background component from the RIDME signal, can be difficult. It has been shown that it is possible to measure Refocused Out-Of-Phase DEER (ROOPh DEER) in which the unmodulated background component is minimal. We have extended this idea to investigate an application of this methodology to the RIDME experiment.



**Figure 1.** 2D frequency-correlated LaserIMD with the fit-detected nitroxide spectrum shown to the left. Lower figure: Frequency dependent slices of the upper figure (thin lines) with corresponding field dependent rectangular pulse detected LaserIMD traces (thicker lines) showing orientation selection.

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## Studying the Conformation of a Receptor Tyrosine Kinase in Solution by Inhibitor-Based Spin Labeling

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Receptor tyrosine kinases (RTKs) are important signalling hotspots in eukaryotic cells. During activation, these molecules undergo large scale conformational changes. In principle, EPR distance measurements are well suited to study the movements of RTKs. However, the many intrinsic cysteines, which can typically be found in such receptors, exclude traditional spin labelling approaches. But, due to the fact that RTKs are among the most important anticancer drug targets, many highly specific inhibitors for these molecules are available. Here, we report a new spin label based on PD168393, a covalent inhibitor of the epidermal growth factor receptor (EGFR). The label facilitates the analysis of the EGFR structure in solution by pulsed electron paramagnetic resonance (EPR) spectroscopy. For various EGFR constructs, including near-full-length EGFR, we determined defined distance distributions between the two spin labels bound to the ATP binding sites of the EGFR dimer. The distances are in excellent agreement with an asymmetric dimer of the EGFR. Based on crystal structures, this dimer had previously been proposed to reflect the active conformation of the receptor but structural data demonstrating its existence in solution have been lacking. More generally, our study provides proof-of-concept that inhibitor-based spin labeling enables the convenient introduction of site-specific spin labels into kinases for which covalent or tight-binding small-molecule modulators are available.

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## Simulating the Whole of Magnetic Resonance

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In a couple of years from now, we will finish kernel programming for *Spinach* – a spin dynamics simulation library that supports all types of magnetic resonance spectroscopy, from  $\text{Gd}^{3+}$  DEER, through DNP and NMR, and all the way to singlet state diffusion MRI, including chemical kinetics, optimal control, and advanced relaxation theories. This level of generality hinges on:

The ability to treat classical degrees of freedom (diffusion, hydrodynamics, radiofrequency and microwave phases, stochastic tumbling, *etc.*) at the same conceptual level as spin degrees of freedom – the corresponding classical equations of motion must be integrated into the density matrix formalism.<sup>[1]</sup>

The ability to survive enormous Kronecker products. A well digitised medical phantom would have at least a hundred points in each of the three directions, meaning a dimension of at least  $100^3 = 10^6$  for the spatial dynamics generator matrices. At the same time, a typical radical contains upwards of ten coupled spins, meaning a Liouville space dimension of at least  $4^{10} \approx 10^6$ . Direct products of spin and spatial dynamics generators would then have the dimension in excess of  $10^{12}$  even before chemical kinetics is considered.<sup>[2]</sup>

Code parallelisation over cluster architectures, including the possibility of using a GPU on each node of the cluster. The principal problem is parallelisation mode switching between powder averages, indirect dimensions of pulse sequences, frequency points of frequency domain simulations, *etc.* – each simulation type would in general require a different mode of parallelisation and GPU utilisation.

This report is about solving all of this, and on where the dark art of simulating a time-domain magnetic resonance experiment stands at the moment. Two recent innovations are the abandonment of Liouville equation in favour of Fokker-Planck equation<sup>[1]</sup> as the core formalism, and the use of tensor structured objects that never open Kronecker products.<sup>[2]</sup> A separate story is recent GPUs: NVidia Tesla V100 performs  $\sim 10^{13}$  double-precision multiplications per second – an astounding amount of computing power that is surprisingly easy to use.

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## Tryptophan Radical EPR Spectra: The $g$ -Values Revised

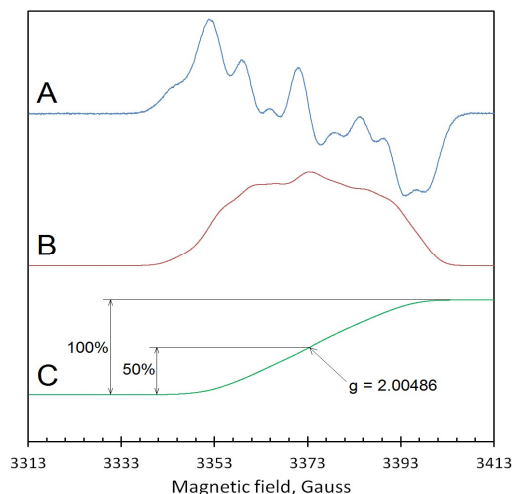
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In 2017, we suggested an algorithm for simulation of the EPR spectra of protein radicals located on tryptophans.<sup>[1]</sup> The algorithm is similar to and based on the well verified by now algorithm for tyrosyl radicals.<sup>[2]</sup> Both Tyrosyl and Tryptophanyl Spectra Simulation Algorithms (TRSSA-Y and TRSSA-W) use empirical relationships linking all Hamiltonian parameters needed for simulation of the EPR spectra with only two input parameters.

We have recently encountered in our research a new protein radical (Figure 1) which we were not able to simulate using TRSSA-Y but which we successfully simulated using TRSSA-W, thus allowing us to assign the radical to a tryptophan. However, we had to introduce a correction (a 3.5 G shift of the experimental spectrum along the magnetic field axis) to produce a nice fit between simulated and experimental spectra. We note now that a smaller correction but of the same direction (sign) has been introduced to our previous tryptophan spectra simulations,<sup>[1]</sup> which at the time we considered as an acceptable discrepancy.

We now believe that discrepancy is not acceptable and explore the possibility that TRSSA-W<sup>[1]</sup> calculates the  $g$ -values of Trp radicals incorrectly. The formulas embedded in original TRSSA-W for  $g$ -values calculations were based on the trends determined from the DFT calculations and the absolute values reported for H-bonded and non-bonded Trp radicals in azurin mutants, when measured directly by high field EPR spectroscopy.<sup>[3]</sup> We will discuss the possibility that the  $g$ -values of the Trp radical have been measured with an error and will present a new, revised version of TRSSA-W which allows simulation of tryptophan radical X-band spectra without the correcting shift along magnetic field axis.



**Figure 1.** The median  $g$ -value of a Trp radical is different from the reported average  $g$ -value determined by the high field EPR (vertical line). A – X-band 10 K spectrum of the Trp radicals formed in bacterioferritin +  $\text{H}_2\text{O}_2$ ; B – its integral; C – its second integral.

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## Topological Spin-Active Sites in Graphenoid Molecules

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Numerous theories have proposed the idea of introducing spins in carbon nanostructures using the topological structure of the carbon lattice. Due to the very low spin-orbit coupling and hyperfine interaction, carbon devices would be more suitable than standard semiconductors to protect coherence and enable long spin transport. However, experiments involving fullerenes and carbon nanotubes yielded negative results showing how the coherence is affected by additional environmental factors.<sup>[1]</sup> Nanographene demonstrated to be a system of interest thanks to the topological protected spin states at the edge. Bottom-up chemical design of the molecules produced defect-free structures that can be functionalised to achieve targeted properties.<sup>[2]</sup> Here, we present the study of the quantum properties of a polycyclic aromatic hydrocarbon (PAH) that shows a singlet ground state and a closely-lying excited triplet state with superior quantum properties. We used pulsed electron paramagnetic resonance to measure the coherence time and evaluate the sources of decoherence in the different regimes. The results suggest better performances than state-of-the-art molecular nano-systems and pave the way to quantum applications of nanographene.

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## Ligand Radicals as Electron Spin Qubits

Jake McGuire,<sup>1</sup> Haralampos N. Miras,<sup>1</sup> James P. Donahue<sup>2</sup> and Stephen Sproules<sup>1</sup>

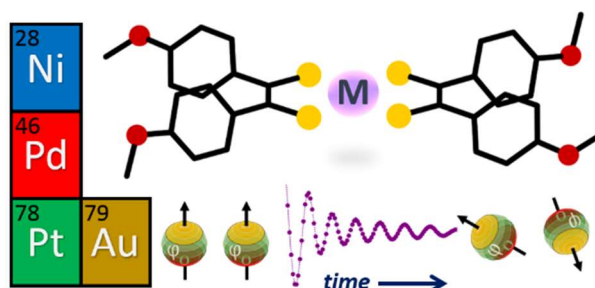
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Electron spin host molecules may be used as qubits, the simplest case being  $S = 1/2$  molecules. This is easily achieved using transition metal complexes.<sup>[1]</sup>

Tris(dithiolene) and bis(dithiolene) complexes have been identified as promising candidates for use as qubits.<sup>[2,3]</sup> However, these studies have centred around the isolation of the electron spin from nuclear spins in the surrounding spin bath to optimise coherence times and have shown little focus to forming multiqubit systems required for gating.

In this study the ligand bis(*p*-anisyl)-1,2-ethenedithiolate (adt) has been used to complex group 10 and 11 metals to form homoleptic ligand radical compounds and diradical heteroleptic phosphine (adt) complexes which have been assessed as electron spin qubits (Figure 1).<sup>[4,5]</sup> The homoleptic complexes are compared with each other and the neutral  $S = 1/2$  [Au(adt)<sub>2</sub>] investigated as a solid state molecular semiconducting qubit when doped in the diamagnetic [Ni(adt)<sub>2</sub>] host. Furthermore, by using (adt) as a ligand radical we show facile synthesis of diradical complexes exhibiting the longest relaxation times in a transition metal complex two qubit system, paving the way to heterometallic and multi-qubit spin systems.



**Figure 1.** The transition metals utilised in bis(adt) with a pictorial representation of decoherence time.

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## Characterization of Liquid-Liquid Phase Separation of FUS with EPR Spectroscopy

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Intrinsically disordered proteins (IDPs) and intrinsically disordered regions (IDRs) do not adopt a well-structured three-dimensional fold.<sup>[1]</sup> IDPs and IDRs are often involved as main actors in protein-protein or protein-RNA/DNA interactions and are drivers of stress granule assembly through liquid-liquid phase separation. However, often, little is known about these systems at the molecular level. Characterization of the conformational ensemble of IDPs and IDRs is a major challenge. EPR in combination with site-directed spin labelling has gained recognition as a tool that provides information on side chain dynamics and distance distributions between two paramagnetic centers.<sup>[2]</sup> Here, we present an approach to characterize the low-complexity domain of the RNA/DNA-binding protein FUS in its dispersed state and during liquid-liquid phase separation. FUS localizes to stress granules, which are membraneless organelles formed upon cellular stress.<sup>[3]</sup> In vitro, monomeric FUS can liquid-liquid phase separate to liquid droplets, which can mature to hydrogels and fibrils. Mutations associated with the neurodegenerative diseases ALS and FTLT lead to irreversible stress granule formation and exacerbate the liquid-to-solid transition in vitro.

Methodology for the studies of these dynamic protein assemblies in vitro with EPR spectroscopy includes CW EPR at ambient temperature, and pulse dipolar spectroscopy measurements at cryogenic temperatures. Singly spin labeled FUS is used to elucidate mobility changes during phase separation at different temperatures with CW EPR spectroscopy. DEER measurements of singly and doubly spin labeled FUS of these heterogeneous systems represent a major challenge and promise to deliver microscopic information on these dynamic protein assemblies. In this presentation, we will discuss the design of site-directed spin labeling for FUS, as well as the first ambient- and low-temperature EPR results, demonstrating the applicability of EPR spectroscopy to study such disordered systems at the molecular level.

This work is supported by the Sinergia grant CRSII5\_170976 from the Swiss National Science Foundation.

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## Non-uniform Electronic Delocalisation in the Radical Cations of Porphyrin Molecular Wires

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The *meso-meso* wiring between porphyrin molecules through single ethynyl linkages has been proven to greatly facilitate the electronic communication between the chromophores. This enhanced electronic communication is evidenced by their unique behaviour as near infrared dyes, and electron-conducting molecular wires.<sup>[1–3]</sup> Maximising the extent of electronic delocalization within these  $\pi$ -conjugated materials is crucial for their optimisation as organic semiconductors with high charge mobility.

EPR has successfully been used to investigate the delocalization of the spin density in a wide range of paramagnetic porphyrin systems such as radical cations and anions,<sup>[4–6]</sup> and photoexcited triplet states,<sup>[7,8]</sup> of cyclic and linear oligomers. In previous studies of the radical cations of ethyne-linked porphyrin oligomers, the largest spin density delocalization length observed at room temperature, which intrinsically correlates with charge mobility along the oligomer chain, spanned over up to seven porphyrin units (*i.e.* >7.5 nm), which is larger than for any other  $\pi$ -conjugated material in solution.<sup>[4–6]</sup> These results were based on the narrowing of the linewidth of the continuous wave (cw) EPR signature of the radical cations as the oligomer chain length was increased up to the heptamer. This method for interpreting cw-EPR spectra is based on the theory proposed originally by Norris in 1971.<sup>[9]</sup>

In this work, we investigate the electronic delocalization of the radical cations of ethyne-linked porphyrin wires which are obtained by chemical oxidation. Initially, the charge mobility along this series is determined by indirectly measuring the isotropic hyperfine couplings to <sup>14</sup>N nuclei using room temperature cw-EPR at X-band (9.4 GHz). The spin density delocalization is then probed by directly measuring the <sup>1</sup>H hyperfine couplings using pulsed ENDOR at Q-band (34 GHz) at cryogenic temperatures. The experimental results are further reconciled with the spin densities and hyperfine couplings obtained from DFT calculations.

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## Improving the Sensitivity and Utility of Pulsed Dipolar Experiments in EPR at 94 GHz

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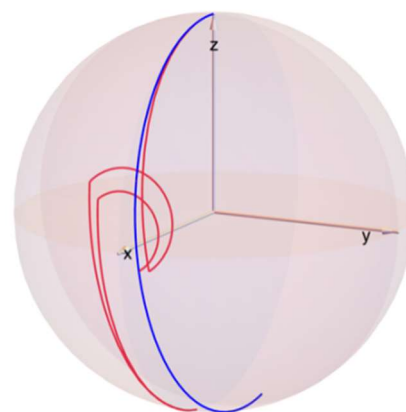
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This talk will present a number of methodological and instrumental techniques to improve the sensitivity and utility of pulsed dipolar spectroscopy (PDS) experiments using the home-built high power spectrometer, HiPER, operating at 94 GHz. These include the implementation of fixed amplitude phase-modulated composite pulses, which correct for imperfections arising due to applied field inhomogeneity, and offer increased excitation bandwidths in comparison with standard pulses.

Using such techniques we demonstrate sensitivity enhancements of more than 30 times on PDS experiments between nitroxides and low-spin Fe(III) centres in haem-proteins, corresponding to reduction in averaging time of almost 1,000 times in comparison to standard commercial spectrometers operating at X-band.<sup>[1]</sup> The use of composite pulses in PELDOR experiments on nitroxide biradicals at W-band were also investigated, including their limitations due to intramolecular effects.<sup>[2]</sup> We also discuss the single-frequency dipolar modulation experiment, RIDME, and how high-field measurements can be utilised to determine both the distance and relative orientation of a cobalt-nitroxide system for the first time.<sup>[3]</sup>



**Figure 1.** Diagram illustrating the rotation of a spin experiencing the effects of applied field inhomogeneity and frequency offset with a standard pulse (blue) and a composite pulse (red).

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## Multidisciplinary Approaches to Structural Investigation: The Nucleosome its Construction and its Remodeling

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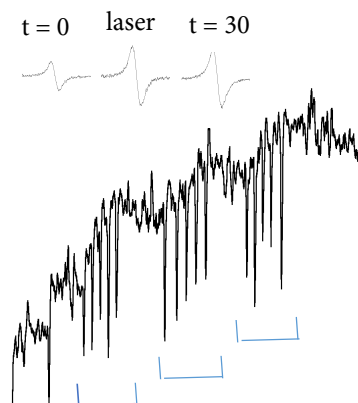
We have used a number of biophysical methods, including EPR, to investigate aspects of the way in which proteins interact with the nucleosome. We have gone from the simplest nucleosome structure, the tetrasome, to investigating the way that histone chaperones interact in the recycling or de novo construction of nucleosomes during genome replication. We have studied one of the proteins involved in nucleosome remodeling (Chd1) both as a free protein as its docked nucleosome complex. The ATP dependent mechano-chemical manipulation of the nucleus during remodeling has been studied using EPR and cryoEM with crucial information being derived on the ATP dependent movement of the CHd1 during the DNA translocation event.

## Interaction Between 694 nm Red (Ruby) Laser Photons and a Static Magnetic Field – Evidence for Charge and Therefore Photon Mass?

Rachel Haywood

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In 1998, I irradiated human skin and hair *in situ* in an ESR spectrometer. Then it was unusual to fire laser photons into the ESR cavity and the applied magnetic field. One of two papers published from this work,<sup>[1]</sup> included a time scan (Figure 1) of laser-irradiated solid hair showing an increase of a stable radical in eumelanin from absorption of red laser photons. At the time I also observed a momentary ‘off-resonance’ of the microwave absorption, or downwards spike, coinciding with the firing of the laser. Chemical reaction of transients formed from photon absorption by hair eumelanin would result in loss of absorption; however, stable radicals were being formed with time and microwave absorption by the radical was restored immediately, and reproducibly after each laser pulse. I have reflected since, whether I observed an interaction between magnetic laser photons and the applied magnetic field, from a fortuitous combination of coherent photons in phase, being absorbed into solid state eumelanin - an efficient UV and visible light absorbing molecule. In a review in 2005, Tu, Luo and Gillies discussed the possibility of finite photon mass.<sup>[2]</sup> I wondered then whether to report my observation to the scientific community, but being neither a physicist or mathematician had my reservations. From a chemical perspective, photons are better described as particles than waves. They are absorbed by matter to become integrated with the electronic structure of atoms or molecules, leading to the formation of excited states which can have an unpaired spin (free radical) or magnetic moment. One explanation of my 1998 observation is that absorption of coherent photons results in the formation of melanin triplet states which are aligned and the melanin particles therefore briefly have a net magnetism. However, I also question and discuss whether this could be evidence for massive, electric charged and magnetic nature of the photon since a change in net melanin magnetism would reflect the absorption of magnetic particles with mass



**Figure 1.** ESR field scans (above) of solid brown/black human hair (10 mg) containing eumelanin before and after 694 nm laser irradiation. Below - time scan (335 seconds) at constant magnetic field for resonance of the stable laser-induced radical. The hair was subject to groups of five laser irradiation pulses (indicated by square brackets) of energy  $18 \text{ J cm}^{-2}$  during the scan.

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## Exploiting Radical Triplet Pair Hyperpolarization: Sensitivity Enhancement in Solution-State NMR

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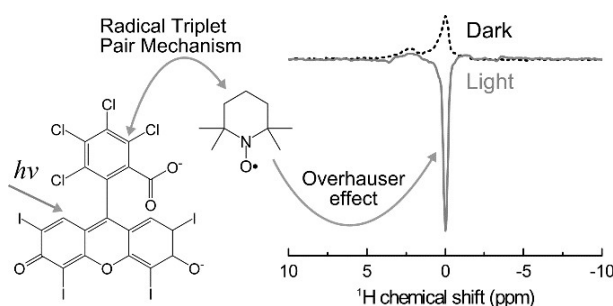
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DNP-NMR methods tackle the low thermal polarization of nuclear spins by microwave-pumped polarization transfer from more strongly polarized electron spin systems, yet in most cases thermal electron spins are used. Significantly larger enhancements, exceeding the 660-fold ( $\gamma_e/\gamma_H$ ) limit, are potentially possible using hyperpolarized electronic spin states as are generated optically via the mechanisms of Spin Chemistry. The use of optically generated electronic hyperpolarization arising through a radical pair mechanism to provide

selective NMR signal enhancements in photo-CIDNP is already well known.<sup>[1]</sup> We recently demonstrated an alternative method (Figure 1), using electronic hyperpolarization arising through a radical-triplet pair mechanism (RTPM) to provide bulk sensitivity enhancements in solution-state NMR.<sup>[2]</sup> Whereas photo-CIDNP typically relies upon a spin-selective photochemical reaction of a triplet with specific amino acid residues (Tyr, Trp and His) the RTPM is a photophysical process that can hyperpolarize extrinsic persistent radicals. As in Overhauser DNP these radicals undergo cross-relaxation, transferring polarization to coupled nuclei with resultant NMR signal enhancements. DNP methods typically involve driving polarization transfer by microwave pumping of electronic transitions. Hyperpolarizing the electron spins by optical pumping could offer much larger enhancements, overcoming the Boltzmann limit, whilst also removing the need for the technically demanding microwave irradiation step as the hyperpolarized radicals undergo cross-relaxation without any further driving radiation.

Here we report recent progress towards increasing the signal enhancement from the RTPM-NMR method. Utilizing recent kinetic studies in our numerical modelling enables an excellent fit to time-resolved EPR data, and through correlating EPR and NMR measurements we have identified conditions that maximize the optical DNP enhancement. Our previously reported enhancements have thus been exceeded by using fully protonated solvents of optimal viscosity in place of partially deuterated solvents.<sup>[2]</sup> Furthermore, numerical exploration of the accessible parameter space has recently identified a potential order of magnitude increase in the obtainable enhancement through minor modification of the experimental conditions.

We thank the Engineering and Physical Sciences Research Council for financial support (EP/N007875/1), and Bruker UK for an equipment loan.



**Figure 1** Optically generated triplets hyperpolarize persistent radicals, which by cross-relaxation enhance <sup>1</sup>H NMR signals in aqueous solution.

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## A Gadolinium Spin Label with Both a Narrow Central Transition and Short Tether for Use in Double Electron Electron Resonance Distance Measurements

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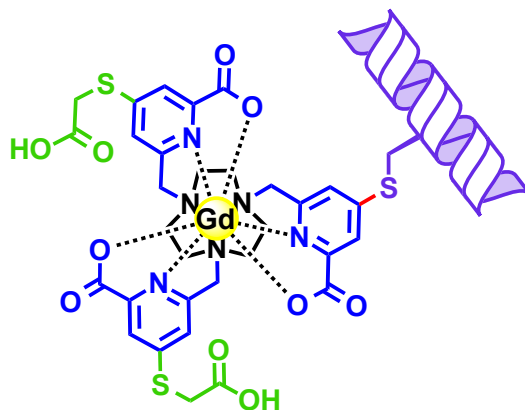
<sup>2</sup> BSRC, University of St Andrews, St Andrews, St Andrews KY16 9ST, UK

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<sup>4</sup> College of Life Sciences, University of Dundee, Dow Street, Dundee DD1 5EH, UK

A gadolinium(III) spin label for proteins has been designed and made, with the aim of increasing sensitivity for DEER measurements through a narrow central transition, long phase memory time and short tether (Figure 1).

The rational, synthesis, characterization, application and DEER results using a Bruker high-power Q-band spectrometer and the St Andrews W-band HiPER spectrometer will be presented. These include a DEER modulation depth of 9% for a 70% labelled protein dimer measured at both EPR frequencies with standard (rectangular) pulses.



**Figure 1.** [Gd.sTPATCN]-SL attached to a cysteine.

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## Measurement of Magnetic Exchange in Asymmetric Lanthanide Dimetallics

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We have been investigating the magnetic interactions between lanthanide ions in a series of isostructural asymmetric dimetallic complexes of dysprosium(III), erbium(III) and ytterbium(III). Using a barrage of techniques including electron paramagnetic resonance spectroscopy, inelastic neutron scattering, and complete active space self-consistent field calculations, we have determined the highly anisotropic magnetic coupling matrix within the low-lying manifold spanned by the ground Kramers doublets of each ion. In all cases the magnetic interaction is not solely dipolar in origin, indicating a measurable superexchange component. We find a unique orientation for the magnetic interaction matrix, corresponding to a common elongated oxygen bridge for the erbium(III) and ytterbium(III) analogues, suggesting a microscopic physical connection to the magnetic superexchange. These results are vital for building and validating model microscopic Hamiltonians to understand the origins of magnetic interactions between lanthanides and how they may be controlled with chemistry.

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## Correlating Exciton Localization and Diffusion with Intermolecular Structure Using Spin Resonance in an Organic Semiconductor

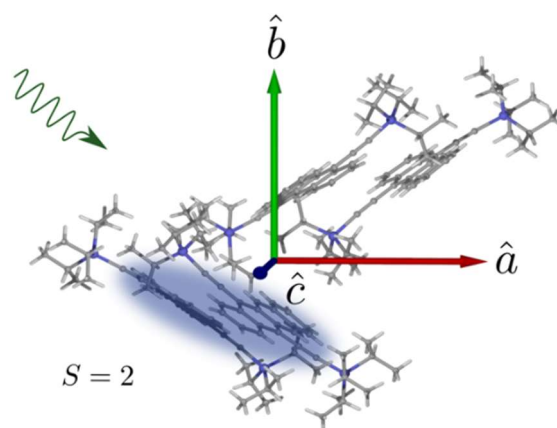
Leah R. Weiss,<sup>1</sup> Kamila Yunusova,<sup>2</sup> Sam Bayliss,<sup>3</sup> Robert Bittl,<sup>3</sup> Richard Friend,<sup>1</sup> Alexei Chepelianskii<sup>2</sup> and Jan Behrends<sup>3</sup>

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In organic semiconductors the exciton pair state is a key intermediate in carrier-multiplication and annihilation. Of particular recent interest is the spin-2 (quintet) bi-exciton, which is comprised of two triplet excitons and can be formed as an intermediate in singlet fission, the formation of two triplet excitons from one singlet excited-state, or in the reverse process of triplet-triplet annihilation.<sup>[1,2]</sup> Of interest for applications in photovoltaics, light-emitting diodes, and photocatalysis, the wavefunction of bi-excitons are difficult to probe experimentally and predict theoretically.<sup>[3,4]</sup> However, the localization of the pair-state is imprinted in the fine structure of its spin Hamiltonian. To access the fine structure of the quintet-state we deploy broadband optically detected magnetic resonance (ODMR) and extract its fine structure and local geometry in an organic semiconductor. We then correlate the experimentally extracted spin parameters with the molecular crystal structure to identify the role of intermolecular geometry in the binding of the exciton-pair. In the same material we correlated ODMR and transient electron spin resonance (trESR) to better understand how the triplet-pair dissociates and diffuses in the molecular lattice.



**Figure 1.** Illustration of the triplet pair state shown in TIPS-tetracene crystal structure with crystal axes shown in red, blue, and green.

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## Quantitative Pulse Dipolar EPR at Submicromolar Concentration Reveals Submicromolar Cu<sup>II</sup>-Affinity of Double Histidine Sites in Proteins

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Electron paramagnetic resonance (EPR) distance measurements can provide highly accurate and precise geometric constraints. This structural information is making increasingly important contributions to studies of biomolecules.<sup>[1,2,3]</sup> Recently, application of double-histidine motifs, coupled with Cu<sup>II</sup>-chelator spin labels shows promise in even higher precision distance measurements, and appeals in systems containing essential cysteines which can interfere with thiol specific labelling.<sup>[4,5]</sup> However, the non-covalent Cu<sup>II</sup> coordination approach is vulnerable to low binding-affinity. Earlier estimations of dissociation constants ( $K_D$ ) revealed high micromolar to low millimolar  $K_D$ s. As many challenging biomolecular targets are only stable at or below low micromolar concentration higher  $K_D$ s are likely to limit the usefulness of this approach.

In this contribution we investigate the binding affinity directly from the modulation-depths of EPR distance experiments.<sup>[6–8]</sup> By combining spectroscopically orthogonal Cu<sup>II</sup> and nitroxide spin labels and performing RIDME (relaxation induced dipolar modulation enhancement) distance measurements<sup>[9,10]</sup> the uncertainty from speciation of the Cu<sup>II</sup> spin label is largely mitigated. By exploiting the superb sensitivity of this experiment and label combination we could demonstrate significant loading of the double histidine sites at submicromolar concentrations. This study demonstrates that (i) the affinity for Cu<sup>II</sup>-chelators is not limiting for pulse dipolar (PD) EPR studies in the low micromolar range, and that (ii) the combination of 5-pulse RIDME and the orthogonal spin-labels Cu<sup>II</sup> and nitroxide makes submicromolar PDEPR experiments feasible.

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## EPR Insights into the Molecular Gripping Machinery

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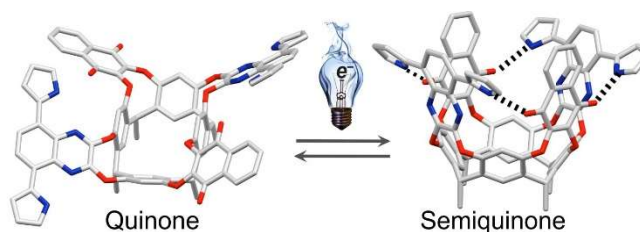
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The control of molecular machines by electrical charge or light is a prerequisite for their application in nanoelectronics. This potential has been uniquely exploited by our groups in a systematic study of quinone-based resorcin[4]arene cavitands.<sup>[1–4]</sup> The cavitands reversibly change their conformation from expanded “kite” to the contracted “vase”, and through the encapsulation of guest molecules in their cavity, can act as molecular grippers.

We have designed, synthesized, and investigated resorcin[4]arene cavitands inspired by the biological role of quinones in photosynthetic reaction centers, where they act as electron acceptors, markedly changing the hydrogen bonding situation, depending on the actual redox state. Cavitands were equipped with alternating quinone and quinoxaline walls, bearing hydrogen bond donor groups (HBD). The aim was to anchor the cavitand “vase” geometry via HB upon reduction to the semi-quinone radical anion (SQ). The SQ state was characterized by a set of electrochemical and spectroscopic methods, involving EPR and UV/Vis spectroelectrochemistry, cw-EPR in liquid and frozen solutions, as well as pulsed EPR and <sup>1</sup>H ENDOR at X- and Q-band frequencies. In the presented contribution the utility of such spectro-electrochemical approach will be discussed, and the prospects of the photoredox-controlled conformational switch in a new generation of molecular grippers will be provided.



**Figure 1.** “Kite” to “Vase” conformational change of the cavitand upon (photo)reduction.

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**POSTER  
ABSTRACTS**

## Hybrid Phenoxyl-Nitroxide Radicals as a New Building Block in Magnetochemistry

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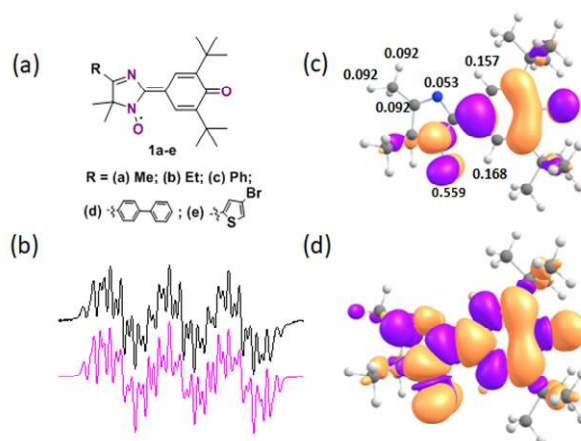
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Resonance stabilized hybrid organic free radicals (HR) seem to be good candidates in design of advanced magnetic materials due to their high level of spin delocalization and, as a result, increasing the possibilities of magnetic coupling through numerous pathways and, consequently, the chance of bulk ordering. However, due to their persistence and complicated synthetic procedures to obtain them, to date only very few examples of HR have been presented in literature.<sup>[1,2]</sup>

Here we describe new stable conjugated all-organic open-shell systems – phenoxyl nitroxide free radicals **1a–e** as a new building block for magnetic materials. The electronic structures of **1a–e** were investigated by a combination of computational (UB3LYP/def2-TZVP) methods and EPR spectroscopy. By EPR, the observed signals consist of a complex multiplets, which can be replicated using a model based on hfs

to couples of distinct <sup>14</sup>N and <sup>1</sup>H nuclei. In the case of **1a,b** the <sup>1</sup>H nuclei of the side methyl and ethyl group should also been taken into account. Calculated spin distributions and hfs constants were in agreement with the values derived from EPR and confirmed the spin delocalization among the whole peripheries of the molecules. Single crystal X-ray diffraction analysis and Broken symmetry (UB3LYP/def2-TZVP) calculations showed arrays of C–O<sub>phenoxyl</sub>...Me<sub>nitroxide</sub> (**1a,b**) or (N)O–C<sub>arom</sub> (**1c–e**) ferromagnetic ( $J_{\text{inter}} = 0.16$  to  $2.21 \text{ cm}^{-1}$ ) 1D chains and C<sub>arom</sub>–C<sub>arom</sub> antiferromagnetic ( $J_{\text{inter}} = -0.7 - -1.4 \text{ cm}^{-1}$ ) dimers (**1c–e**) forming 3D networks through the lattices.

This investigation was supported by RFBR grant no. 17-53-50043 and Ministry of Education and Science of the Russian Federation (state contract no. 14. W03.31.0034).



**Figure 1.** (a) Chemical structures of phenoxyl nitroxides under investigation; (b) experimental (black) and simulated (violet) X-band EPR spectrum of **1a** in toluene at RT; (c) isosurface plot of SOMO and derived hfs constants ( $A_N$  and  $A_H$ ) in mT for **1a**; (d) spin density distribution map for **1a** calculated on UB3LYP/def2-TZVP level of theory.

[1] S. M. Winter, A. R. Balo, R. J. Roberts, K. Lakin, A. Assoud, P. A. Dube and R. Oakley, *Chem. Commun.*, 2013, **49**, 1603.

[2] P. Vasko, J. Hurmalainen, A. Mansikkamäki, A. Peuronen, A. Mailman and H. M. Tuononen, *Dalton Trans.*, 2017, **46**, 16004.



# The Static and Dynamic Electronic and Geometric Structure of Catalysts in Mesoporous Polymers

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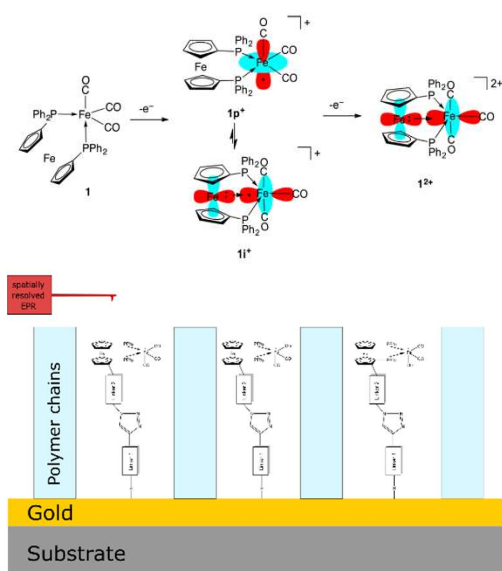
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In contrast to enzymes, organometallic catalysts often show a lack of stereoselectivity and productivity but resource depletion and an increase in environmental restrictions require optimal catalytic processes. In this project, catalysts are introduced into highly defined meso-pores where we expect higher selectivities, arising from the high level of order in the pores and the influence of mesopores themselves. One of the goals is to explore the cooperative effect of the support, as well as the influence of the pore size, pore polarity, tether length and rigidity of the system.

In order to do so, the electronic and geometric structure of the investigated catalyst, (dppf)Fe(CO)<sub>3</sub>, needs to be understood on a fundamental level. This allows the explanation of the structural changes after the introduction into the mesopores.

This system was chosen because it is paramagnetic in its oxidised form, thereby allowing multiple spectroscopic methods which are well established in the group. These include EPR, MCD and SQUID magnetometry. Furthermore, Mössbauer spectroscopy will be a useful tool to investigate and characterise the iron atoms in the molecule. The collected data indicates the occurrence of two isomers of which the temperature dependent ratio was investigated via EPR spectroscopy. In a next step the catalyst is to be linked to the different mesoporous systems, consisting of polymers and covalent organic frameworks. This can be realised through click chemistry via azide groups attached to the catalyst and terminal alkine groups in the mesopores.



**Figure 1.** Simplified orbital structure of the two systems for the singly oxidised and the doubly oxidised species (top),<sup>[1]</sup> and project idea to link the catalyst to the mesoporous structure (bottom).

[1] M. R. Ringenberg, F. Wittkamp, U.-P. Apfel and W. Kaim, *Inorg. Chem.*, 2017, **56**, 7501.

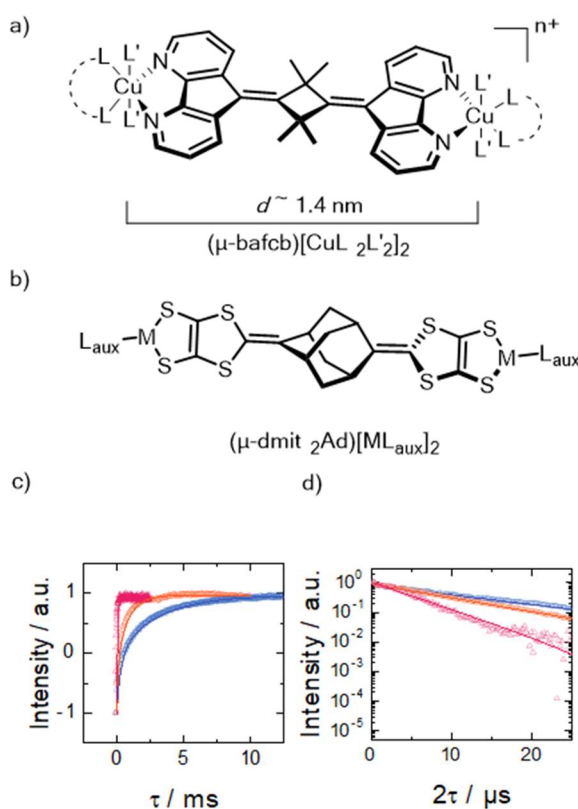
# Novel Potential Multi-Qubit Systems with Very Rigid Bridging Ligands

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As the current semiconductor technology approaches its limits, scientists around the world are looking for solutions to use quantum phenomena for computing purposes. Although theoretically established, a practical application of quantum computing is still very complicated. Two-qubit-based quantum gates needed to complete the ensemble of universal gates<sup>[1,2]</sup> are rare, thus encouraging the hunt for such systems. To use a multi-qubit quantum gate, the dipolar coupling has to be bigger than a typical operation time (approx. 10 ns). As this directly correlates to the distance between the qubits, long bridging ligands are needed. These should be very rigid, ensuring a spatial and electronic separation of the qubits.

Inspired by the work on photo switches from Belser et al.<sup>[3–5]</sup> in the 90's, which incorporate requirements stated above, as well as the recent insights on the potential of nuclear spin-free 1,3-dithiole-2-thione-4,5-dithiolate (dmit) coordination environments,<sup>[6,7]</sup> this project focused on the synthesis and characterization of EPR active coordination compounds with ligands like **bafcb** and **dmit<sub>2</sub>Ad**.



**Figure 1.** a) Cu(II) dimer with **bafcb** as a bridging ligand; b) **dmit<sub>2</sub>Ad** ligand featuring the well-established dmit coordination site, work in progress; c,d) Temperature dependency of  $T_1$  and  $T_m$  of a) with  $L = \text{Cl}$ ,  $L' = \text{Py-d}_5$ ,  $n = 0$  (@ 7K:  $T_m = 13.00(5) \mu\text{s}$ ).

[1] D. P. DiVincenzo, *Fortschr. Phys.*, 2000, **48**, 771.

[2] A. Barenco, C. H. Bennett, R. Cleve, D. P. DiVincenzo, N. Margolus, P. Shor, T. Sleator, J. A. Smolin and H. Weinfurter, *Phys. Rev. A*, 1995, **52**, 3457.

[3] P. Belser, S. Bernhard, C. Blum, A. Beyeler, L. De Cola and V. Balzani, *Coord. Chem. Rev.*, 1999, **190**, 155.

[4] S. Bernhard and P. Belser, *Synthesis*, 1996, 192.

[5] V. Balzani, F. Barigelletti, P. Belser, S. Bernhard, L. De Cola and L. Flamigni, *J. Phys. Chem.*, 1996, **100**, 16786.

[6] M. Atzori, E. Morra, L. Tesi, A. Albino, M. Chiesa, L. Sorace and R. Sessoli, *J. Am. Chem. Soc.*, 2016, **138**, 11234.

[7] C.-J. Yu, M. J. Graham, J. M. Zadrozny, J. Niklas, M. D. Krzyaniak, M. R. Wasielewski, O. G. Poluektov and D. E. Freedman, *J. Am. Chem. Soc.*, 2016, **138**, 14678.

## DEER Measurement Employing for Exploring the Binding Site of Fucose-Functionalized Precision Glycomacromolecules Targeting Human Norovirus Capsid Protein

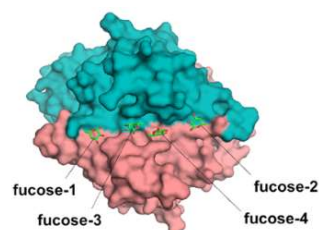
Anna Rubailo,<sup>1</sup> Sabrina Weickert,<sup>1</sup> Katharina Susanne Bücher,<sup>2</sup> Laura Hartmann<sup>2,3</sup> and Malte Drescher<sup>1</sup>

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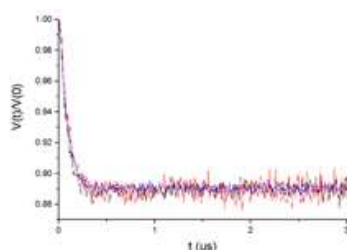
<sup>2</sup> Heinrich-Heine-University Düsseldorf, Institute for Organic Chemistry and Macromolecular Chemistry, Düsseldorf, Germany

<sup>3</sup> Institute of Chemistry and Metabolomics, University of Lübeck, Lübeck, Germany

The nonbacterial gastroenteritis in human mostly is provoked by norovirus infection which belongs to the Caliciviridae family.<sup>[1]</sup> In order to uncover the virus's biological properties with the aim to modify biochemical function of norovirus by inhibitors and prevent infection. To understand the binding mechanism and to design potential ligands to block the norovirus binding sites, it is crucial to identify the involved binding sites for multivalent interactions. The X-ray structure shows distances between the L-fucose binding pockets are estimated to be 11 Å (fucose sites 1 and 3), 17 Å (fucose sites 1 and 4) and 27 Å (pockets 1 and 2; Figure 1).<sup>[2]</sup> Theoretically, divalent glycomacromolecules could bridge the outer binding sites. The glycomacromolecules were synthesized by stepwise assembly of tailor-made building blocks on solid support. Final oligo(amidoamine) scaffold allows for the conjugation of sugar ligands in the side chains.<sup>[2]</sup> We provided structural evidence, by electron paramagnetic resonance (EPR)



**Figure 1.** Structure of NoV GII.10 P-dimer with binding of L-fucose (green sticks) to the four sites.<sup>[3]</sup>



**Figure 2.** DEER distance measurements of the doubly spin-labeled L-fucose ligand in the absence (blue) and in the presence (molar ratio P-dimer/L-fucose ligand 1:4 (red) and 1:1 (black)).

spectroscopy, binding mode of fucosylated precision glycomacromolecules as multivalent model structures for the investigation to Norovirus P-dimers. We used the double electron-electron resonance (DEER, also PELDOR) in combination with site-directed spin labeling, TEMPO side chain, at both ends of the glycomacromolecule. The DEER measurements were performed for the spin-labeled divalent glycomacromolecule in the absence and presence (molar ratio P-dimer/Fucose- ligand 1:4 and 1:1) of the P-dimer (Figure 2). DEER data sets were analyzed using the DeerAnalysis 2016 software package for MATLAB.<sup>[3]</sup> No significant differences in the absence and presence of GII.4 P-dimer were observed for the data obtained in these experiments suggesting that the conformational ensemble of the glycomacromolecule remains unaltered upon interaction with the P-dimer.

- [1] L. C. Lindesmith, E. F. Donaldson, A. D. Lobue, J. L. Cannon, D. P. Zheng, J. Vinje and R. S. Baric, *PLOS Med.*, 2008, **5**, e31.
- [2] K. S. Bücher, H. Yao, R. Creutzmacher, K. Ruoff, A. Mallagaray, A. Grafmüller, J. S. Dirks, T. Kilic, S. Weickert, A. Rubailo, M. Drescher, S. Schmidt, G. Hansman, T. Peters, C. Uetracht and L. Hartmann, *Biomacromolecules*, 2018, **19**, 3714.
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# **$^{17}\text{O}$ High Field ENDOR to Investigate Water-Mediated PCET in *E.coli* Ribonucleotide Reductase**

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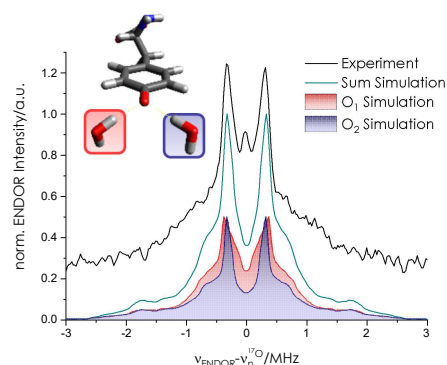
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ENDOR is a powerful tool to probe the ligand sphere of paramagnetic species in a wide variety of observable systems. The  $^{17}\text{O}$  nucleus is a valuable probe for the presence of water but its low gyromagnetic ratio, large nuclear spin of  $I = 5/2$  and large quadrupole couplings make the spectroscopy challenging. It was already extensively employed to investigate the binding of water to transition metal complexes but reports on water binding to protein radicals have been scarce.

Amino acid radicals play an important role in biological electron transfer processes in proteins. Four distinct tyrosyl radicals have been identified as intermediates during the 35

Å proton-coupled electron transfer (PCET) in *E.coli* ribonucleotide reductase, which has been intensively studied as a paradigm for long range protein PCET.<sup>[1]</sup>  $\text{Y}_{356}^\bullet$  has been of particular interest in the last few years, as it is supposed to reside at the subunit interface of the protein active complex and water molecules are expected to facilitate the radical transfer across the interface. A hydrogen bonding network has been detected using  $^1\text{H}$  ENDOR, strongly suggesting the binding of two waters to  $\text{Y}_{356}^\bullet$ .<sup>[2]</sup> However, conclusive evidence for water involvement is missing so far.

Here we present 94 GHz  $^{17}\text{O}$  ENDOR supported by HYSCORE experiments at 1.2 T on a model system for  $^{17}\text{O}$  hyperfine spectroscopy and on  $\text{Y}_{356}^\bullet$  in the active RNR enzyme. The stable nitroxide radical TEMPOL was chosen as a spin probe and investigated in  $\text{H}_2^{17}\text{O}$  (90% isotope labelling). We also present Mims ENDOR of RNR in  $\text{H}_2^{17}\text{O}$  in recorded at 94 GHz (3.4 T) EPR frequency and their simulations compared to small cluster DFT calculations. The results show that  $^{17}\text{O}$ -ENDOR spectroscopy can be used effectively to study water binding to nitroxide radicals. The experiments on RNR show remarkably sharp coupling features, suggesting close binding of two water molecules to  $\text{Y}_{356}^\bullet$  in accordance with our previous experiments.<sup>[2]</sup>



**Figure 1.** 94 GHz  $^{17}\text{O}$  Mims ENDOR and small cluster DFT calculation of tyrosyl  $\text{Y}_{356}^\bullet$  in *E. coli*

[1] E. C. Minnihan, D. G. Nocera and J. Stubbe, *Acc. Chem. Res.*, 2013, **46**, 2524.

[2] T. U. Nick, K. R. Ravichandran, J. Stubbe, M. Kusanmascheff and M. Bennati, *Biochemistry*, 2017, **56**, 3647.

# Theoretical Inspection of Laser-Induced Magnetic Dipole Spectroscopy (LaserIMD)

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LaserIMD allows the determination of distance distributions in the nanometer region between a photo label and a permanent radical.<sup>[1-3]</sup> The photo label is initially diamagnetic and forms a triplet upon photo excitation. In DEER the dipolar information is obtained by a  $\pi$ -pulse that induces a transition of  $\Delta m = \pm 1$  in a pump spin. A similar explanation is true for RIDME where the transitions between the spin states are caused by relaxation.

For LaserIMD the situation is different because the singlet state passes to a superposition of triplet states. As this transition is typically initiated by spin-orbit coupling, the  $T_+$  and  $T_-$  states are equally populated. This results in a net magnetization of zero during the evolution of the dipolar oscillation.

For the calculations we introduced three spins: a permanent radical  $S$  that acts as the observer spin and two spins  $L$  and  $I$  that form the singlet and triplet state of the photo label. We derived the commutation relations according to the product operator formalism and used them to perform an analytical calculation of the LaserIMD pulse sequence. The singlet-triplet transition was introduced by taking the partial trace over the  $L$  and  $I$  states and forming the Kronecker product between the pure density operator of the spin  $S$  and the newly created triplet of the  $L$  and  $I$  spins. This will lead to a transfer of the coherences that have been generated by the initial  $\pi/2$ -pulse, meaning that they change their position in the density matrix. This transfer allows them to undergo a dipolar evolution resulting in the LaserIMD signal.

A calculation in the spin state picture showed that the transition that is responsible for the dipolar signal is between the  $D_{+y}T_x$  and the  $D_{-y}T_y$  state. Here  $D_{\pm y}$  are the eigenstates of the doublet spin  $S$  in the  $y$ -direction and  $T_x$  and  $T_y$  are the zero field eigenstates of the triplet.

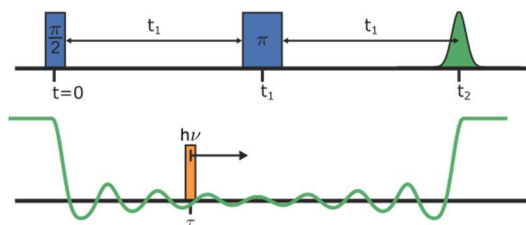


Figure 1. The LaserIMD pulse sequence

[1] C. Hintze, D. Bückner, S. Domingo Köhler, G. Jeschke and M. Drescher, *J. Phys. Chem. Lett.*, 2016, 7, 2204.

[2] A. Bieber, D. Bückner and M. Drescher, *J. Magn. Reson.*, 2018, 296, 29.

[3] M. G. Dal Farra, S. Ciuti, M. Gobbo, D. Carbonera and M. Di Valentin, *Mol. Phys.*, 2018, DOI: 10.1080/00268976.2018.1503749.

## Biophysics in Drug Discovery: Characterization of Ligand-DNA Interactions by NMR Spectroscopy and Isothermal Titration Calorimetry

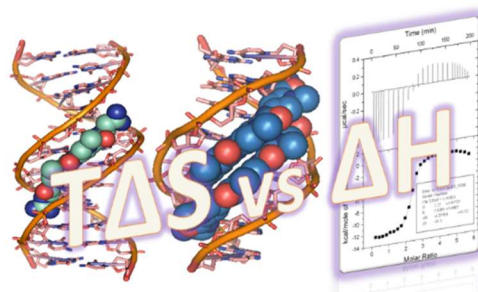
Hasan Y. Alniss<sup>1</sup> and John A. Parkinson<sup>2</sup>

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The cationic lexitropsins, which bind non-covalently to the minor groove of DNA (Figure 1), have shown therapeutic potential in the treatment of cancer, viral and bacterial diseases.<sup>1</sup> Understanding the factors that drive ligand-DNA associations, particularly the structural features, sequence selectivity, molecular forces and the energetics that dictate the overall binding process is of fundamental scientific interest as well as a prerequisite for the rational design and development of novel drugs.<sup>[1]</sup> In this work, a holistic approach was followed to tackle this issue by combining thermodynamic and structural studies to gain insight into the factors that drive lexitropsin-DNA interactions in order to design compounds to target specific genes associated with prostate cancer.

In this study, ligand-DNA associations were characterized by using different biophysical techniques. NMR spectroscopy and restrained molecular dynamics simulations were used to obtain structural details for lexitropsin-DNA complexes. The NMR NOE derived inter-proton distances were used to generate three dimensional structures for these complexes via the restrained molecular dynamic simulations. Isothermal titration calorimetry (ITC) was used to obtain a complete thermodynamic profile for lexitropsin interactions with different ODN sequences and that included the determination of the binding affinity (K), stoichiometry (n), enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy of binding ( $\Delta G$ ).<sup>[2,3]</sup> This study helped to reveal the molecular forces that drive the binding and to establish a link between the structure and the binding affinity by studying the structural and the thermodynamic binding characteristics of closely related ligand structures to a specific binding site. These findings could be useful in the design of novel lexitropsin for therapeutic purposes.



**Figure 1.** Representation of NMR refined structures (left) and ITC characterizations (right) of DNA minor groove binders (MGBs).

[1] H. Y. Alniss, *J. Med. Chem.*, 2019, **62**, 385.

[2] H. Y. Alniss, M. V. Salvia, M. Sadikov, I. Golovchenko, N. G. Anthony, A. I. Khalaf, S. P. MacKay, C. J. Suckling and J. A. Parkison, *ChemBioChem*, 2014, **15**, 1978.

[3] H. Y. Alniss, N. G. Anthony, A. I. Khalaf, S. P. MacKay, C. J. Suckling, R. D. Waigh, N. J. Wheate and J. A. Parkison, *Chem. Sci.*, 2012, **3**, 711.



# ESR Spectroscopy of Structural Phase Transition in $\text{Mn}^{2+}$ Doped $[(\text{CH}_3)_2\text{NH}_2][\text{Cd}(\text{N}_3)_3]$ Hybrid Perovskite Framework

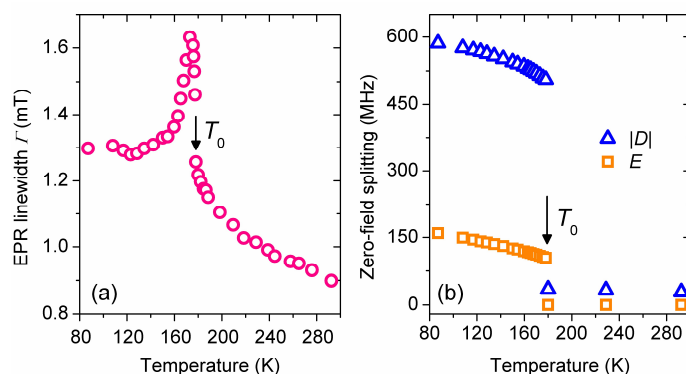
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Hybrid perovskite formate frameworks attracted significant attention of the scientific community due to the indications of the multiferroic behavior.<sup>[1]</sup> These compounds consist of transition metal ions linked by formate groups into porous frameworks, where each pore contains a single molecular cation. The majority of formate frameworks exhibit structural phase transitions, which involve long-range molecular cation ordering and metal-formate framework deformation.

Here we employ CW ESR spectroscopy to study a structural phase transition in a novel  $[(\text{CH}_3)_2\text{NH}_2][\text{Cd}(\text{N}_3)_3]$  (DMACd) hybrid formate framework<sup>[2]</sup> doped with a tiny amount of  $\text{Mn}^{2+}$  ions. The temperature dependent ESR spectra of DMACd: $\text{Mn}^{2+}$  powder prove successful replacement of the  $\text{Cd}^{2+}$  ions and formation of the  $\text{MnN}_6$  octahedra. Upon cooling, ESR spectra exhibit drastic changes at the transition temperature of 178 K demonstrating that the  $\text{Mn}^{2+}$  centers are susceptible to the structural changes occurring during the phase transition. An anomalous behavior of the CW ESR linewidth and zero-field splitting of the  $\text{Mn}^{2+}$  probes at the phase transition point indicates strong first-order character of the phase transition in DMACd (Figure 1).



**Figure 1.** Temperature dependences of (a) the peak-to-peak CW ESR linewidth of the  $m_I = -5/2$  hyperfine line, and (b)  $D$  and  $E$  zero-field splitting parameters of the  $\text{Mn}^{2+}$  centers in DMACd.

[1] P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby N. S. Dalal, H. W. Kroto and A. K. Cheetham, *J. Am. Chem. Soc.*, 2009, **131**, 13625.

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## EPR and Hyperfine Spectroscopy Study of the Metallochaperones Assisting the Cu<sub>A</sub> Center Assembly on Cytochrome Oxidase

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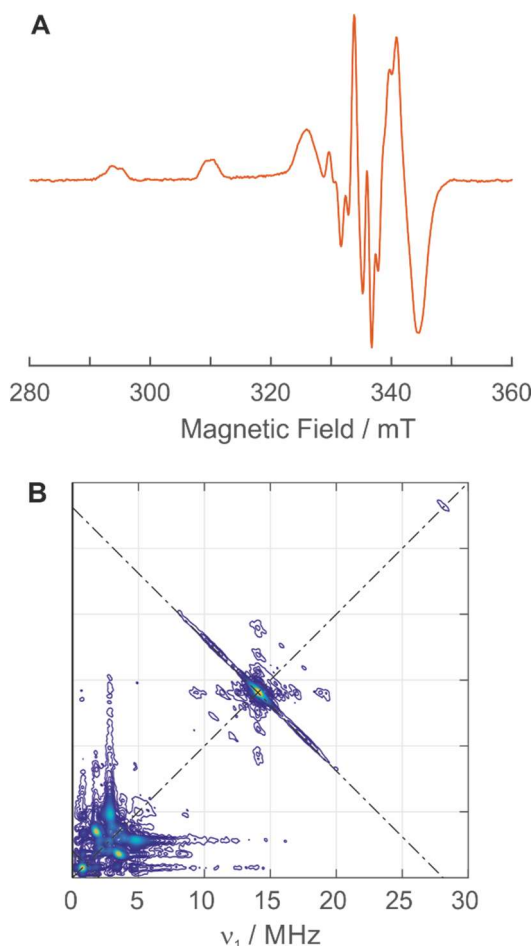
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The cellular reaction of oxygen reduction to water, essential for most eukaryotic life, is catalyzed by cytochrome *c* oxidase, a multi-subunit transmembrane metalloenzyme complex. This machine is assembled and equipped with its metal cofactors in a highly concerted process involving a network of proteins responsible for membrane insertion and delivery of metal ions by metallochaperones to form the active sites. Here we focus on the formation mechanism of the binuclear copper Cu<sub>A</sub>-site in subunit II of cytochrome *c* oxidase (CoxB), for which in *Bradyrhizobium diazoefficiens* three proteins are known to be responsible, the two copper chaperones ScoI and PCuC as well as TlpA, a thioredoxin-like protein that reduces the cysteine pairs in the copper binding sites of CoxB and ScoI.<sup>[1]</sup>

Using a variety of biophysical and biochemical techniques, we found that the initial step, the delivery of the first copper ion is carried out by ScoI, which forms a complex with CoxB. Subsequently, another copper ion is delivered by the Cu-chaperone PCuC. Using EPR spectroscopy we follow copper insertion into CoxB and the formation of the Cu<sub>A</sub>-site. Our results aid to clarify the role of the copper chaperones involved and to suggest a novel mechanism for the Cu<sub>A</sub>-site formation.

Initial characterization of isolated intermediates, such as the ScoI:CoxB complex, provided well-resolved EPR spectra (Figure 1) and features of the local Cu(II) coordination that are further characterized by hyperfine spectroscopy with the aim to identify protein residues contributing to Cu(II) coordination in the future.



**Figure 1.** Cu(II) chaperone ScoI in complex with CoxB, (A) low-temperature cw EPR spectrum and (B) 3- $\tau$  HYSCORE spectrum.

[1] H. K. Abicht, M. A. Schärer, N. Quade, R. Ledermann, E. Mohorko, G. Capitani, H. Hennecke and R. Glockshuber, *J. Biol. Chem.*, 2014, **289**, 32431.

## Multi Frequency Orientation Selective Copper(II) Nitroxide RIDME in Model Systems and Proteins

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Metal ions play an important structural and functional role in metalloproteins. PELDOR (Pulsed electron-electron double resonance) has been extensively used to measure distances involving metal ions and to localise them within the global fold of a protein.<sup>[1]</sup> Moreover, distance measurements by PELDOR can inform on the orientation between the spin centres and the inter-spin vector adding valuable angular constraints to the distance information.<sup>[2–4]</sup> Nevertheless, PELDOR measurements involving metal ions with fast relaxation times and broad spectra are demanding. On the other hand, the single frequency RIDME (relaxation induced dipolar modulation enhancement) technique can increase sensitivity and with longitudinal relaxation of the metal centred spin replacing the pump pulse, it can become more suitable than PELDOR for distance measurements involving metal ions.<sup>[5]</sup> The feasibility of orientation selective (OS) RIDME was demonstrated on a low-spin Co(II) complex containing two nitroxide (NO) labelled terpyridine ligands yielding the relative orientation between the inter-spin vector and the nitroxide g-tensor.<sup>[6]</sup> Here, we extended this work to OS RIDME on the analogous Cu<sup>II</sup> complex<sup>[7]</sup> at Q-, W- and J-band. Furthermore, the OS RIDME is extended to a singly spin-labelled model protein that has Cu(II)-nitrilotriacetic coordinated to a double histidine (dHis) site.<sup>[8]</sup> Two different constructs are investigated and we will present initial OS Cu(II)-nitroxide RIDME data on a protein system as well as report on progress with OS multi-frequency RIDME.

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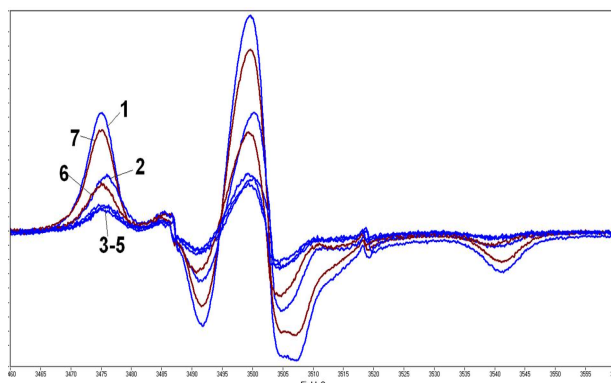
## Processes Mediated by Encapsulated AuNP in Polymeric Gels Evidenced by EPR Spectroscopy

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Gold nanoparticles (AuNP) have been investigated for decades as selective catalysts for a series of reactions such as alcohol oxidation. In solution, AuNP are commonly stabilised by various protecting groups, but this hinders their use as catalysts. Therefore, the nanoparticles need to be supported. Numerous studies indicate the use of inert inorganic supports such as silica, ZnO and TiO<sub>2</sub>.<sup>[1]</sup>

In recent years, hybrid organic/inorganic materials have been gaining enormous attention.<sup>[2]</sup> The easiest way to prepare nanoparticles with well-defined dimensions is by encapsulating them in gels, but this method is not successful in all cases. In this study, we used the less common method to obtain hybrid hydrogel/AuNP by reducing of gold salt *in situ*.<sup>[3]</sup> To evidence the properties of reduction/oxidation in these materials, we used spin-labelled polysaccharide hydrogels. Figure 1 shows the evolution of the EPR spectra for a spin-labelled hydrogel during the formation of AuNP in the hydrogel matrix. In the poster will be presented the results obtained on nitrophenol reduction and alcohols oxidation by using as catalyst AuNP embedded in hydrogels.



**Figure 1.** The EPR spectra of spin-labelled hydrogel: (1) initial, (2–5) after the diffusion of the gold salt and the start of the reduction process, and (6,7) after the formation of

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## Evolution of Free Radicals from a Novel Pt(IV) Mono Azido Complex Following Irradiation with Visible Light

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Platinum-based anticancer drugs, e.g. cisplatin, are widely used in chemotherapy, but their non-specificity and high cytotoxicity often lead to side-effects.<sup>[1]</sup> Photo-Activated Chemotherapy (PACT), where a stable prodrug is selectively accumulated in the target cells prior to photoactivation of its cytotoxicity, is an attractive alternative to avoid side-effects.<sup>[2]</sup> Promising PACT prodrugs include diazido Pt(IV) complexes like [*trans,trans,trans*-Pt(N<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(py)<sub>2</sub>] (**1**; Figure 1), which has been previously shown to reduce to the DNA-crosslinking species Pt(II) and to release azidyl radicals, hydroxyl radicals and singlet oxygen, under visible light illumination.<sup>[3-5]</sup>

Identification of the radical species released on illumination is important in helping to understand the phototoxicity of PACT drugs. Here we present a continuous wave EPR study under different conditions using spin-trapping to identify the radicals formed on illumination of a novel Pt(IV) mono azido mono triazolato complex (**3**; Figure 1). In MeCN-*d*<sub>3</sub>, complex **3** exists as an equilibrium mixture between two species (**3a** and **3b**) under rapid interconversion, and is stable in solution for >6 months. In contrast, complex **3** is unstable in D<sub>2</sub>O, slowly undergoing conversion to a new species. CW-EPR spin trapping experiments with DMPO in aqueous solution revealed the release of both azidyl and hydroxyl radicals from complex **3** when irradiated with blue light. By comparison, no hydroxyl radicals (only azido radicals) were observed when **3** was irradiated in acetonitrile. Understanding the solution photochemistry observed for complex **3** may enable us to better understand the photocytotoxic role and relative importance of the azidyl and hydroxyl radicals when released *in cellulo*.

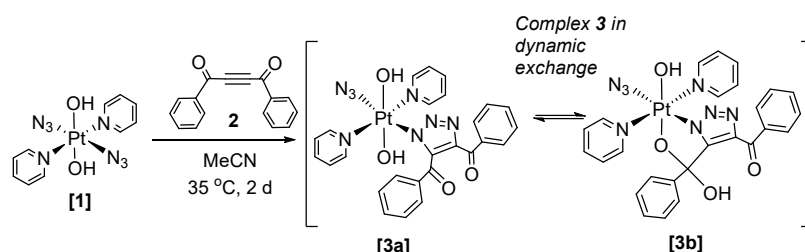


Figure 1. Synthetic route to complex 3

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## ***In-situ* EPR/UV-Vis-NIR Spectroelectrochemistry of Thienoacene-Extended Tetrathiafulvalenes**

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Tetrathiafulvalene (TTF) is an effective  $\pi$ -electron-donating molecule that displays unique electrochemical behavior. A characteristic feature of TTF is that, upon stepwise oxidation, it gives rise to two sequentially oxidized species, namely, the TTF radical cation (TTF<sup>•+</sup>) and the TTF dication (TTF<sup>2+</sup>).  $\pi$ -Dimerization of tetrathiafulvalene (TTF) radical cations has become an important tool in supramolecular chemistry owing to the ability to turn on and off this association by reversible oxidation of TTF. The  $\pi$ -extended TTF analogues subject of interest are the diindenothienoacene-tetrathiafulvalenes with one, two or three fused thiophene rings as  $\pi$ -conjugated spacers between the two DTF units. DTF units are either positioned next to the sulfur in the nearest thiophene unit or are placed opposite to the sulfur.

$\pi$ -Dimerization can be followed by cyclic voltammetry and optical spectroscopy measurements. In situ EPR/UV-Vis-NIR spectroelectrochemical studies were performed to obtain a more detailed description of the influence exerted by one or more central thiophene rings and the influence of connecting the two dithiafulvene units in a cross-conjugated or linearly conjugated manner.<sup>[1]</sup> ESR spectroelectrochemical studies of some studied complexes, reveals two slightly different ESR signals upon oxidation, one assigned to the mixed-valence (MV) dimer and the other to the cation monomer. For another samples, interestingly three different EPR spectra were observed upon oxidation. In the region where the cation radicals dominate, a new broadened EPR spectrum with  $g$ -value of 2.0056 appears, and simultaneously the UV-Vis-NIR spectra show two strong maxima at 650 nm and 1010 nm. These species could possibly be ascribed to a TTF<sup>•+</sup>...TTF<sup>•+</sup> biradical species confirming the strong association between radical cations in this case. Also, the calculations reveal that the triplet ground state is more stable than the singlet ground state for doubly charged large conjugated systems. Going to the region of the second electron transfer, the concentration of such species strongly decreases, and remaining isolated cations exhibits a strongly shifted  $g$ -value of  $g = 2.0063$ , which confirms a lower delocalized spin in comparison to both the TTF...TTF<sup>•+</sup> and TTF<sup>•+</sup>...TTF<sup>•+</sup> associates.

The authors acknowledge the support of Slovak Research and Development Agency (APVV-15-0053), Slovak Scientific Grant Agency VEGA (1/0416/17, 1/0466/18).

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## Prospective Copper(II) Metallodrugs with Redox Cycling and Intercalating Functionalities

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Attention has been paid to the design of novel bifunctional metal complexes with the intention to develop a new class of metal-based anticancer drugs which possess higher efficacy compared to cis-platin derivatives.<sup>[1]</sup> In line with this, a novel series of Cu(II) complexes with NSAIDs (tolfenamic, mefenamic and flufenamic acids) and 1,10-phenantroline has been prepared. We focused on the detailed structural characterization and biochemical evaluation to find a correlation between electronic structure and biological activity. To describe the bonding properties, X-ray structure analysis and EPR spectroscopy were performed. Hirshfeld surface analysis was used to study the intermolecular interactions within the crystal structure of Cu(II) complexes.

X-band EPR spectra of Cu(II) complexes were studied as polycrystalline solids and in DMSO frozen solutions. As expected, the EPR spectra measured as frozen solutions were better resolved than those recorded from solid state samples. An investigation was made to see whether the geometry around copper ion is influenced by the presence of the solvent especially when strongly coordinating solvents are present, such as DMSO. Structural stability in solution determines biological application, since “in vivo” reactions are carried out in fluids. EPR measurements revealed complexes with a distorted bipyramidal coordination around the copper(II) ion.

Based on the similarity of the EPR data obtained from two phases, it could be concluded that the Cu(II) complexes in DMSO retain similar geometry as in the solid state. Surprisingly the EPR spectrum of complex containing flufenamic acid, exhibit five lines in parallel hyperfine splitting pattern, which corresponds to two slightly different coordination around copper ion. Upon cooling to 210 K this pattern collapsed into usual four line set, which indicates the phase transition occurred. Using an iterative solution of a set of equations that connect the spin Hamiltonian parameters and *d-d* transitions obtained from the electronic spectra, we were able to estimate values of the molecular orbital coefficients which characterize the degree of covalency the  $\sigma$ -plane,  $\pi$ -in-plane, and  $\pi$ -out of plane bonding, respectively.

Interaction with DNA was tested by means of viscometric measurements in which intercalation toward plasmid DNA pBSK+ was proven. Following the interaction of the complexes with superoxide radical anions, reduction of Cu(II) to Cu(I) occurs. It was documented by the application of a specific chelator of Cu(I) species, neocuproine, and from EPR measurements. Prepared Cu(II) complexes exhibit an excellent SOD-mimetic activity and promising selective anticancer activity against several cancer cell lines.<sup>[2]</sup>

This work was supported by Scientific Grant Agency VEGA Projects 1/0686/17.

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## EPR Spin Trapping Technique as a Useful but Tricky Tool in the Studies of Photoinduced Processes

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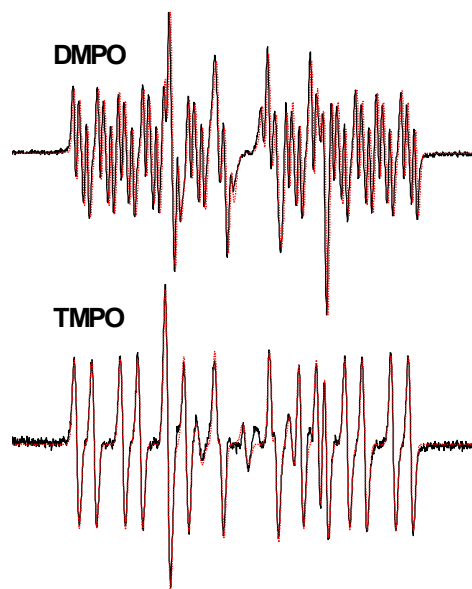
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Photoinduced processes taking place in the heterogeneous or homogeneous systems often involve the formation of reactive radical intermediates. Either we talk about the reactive oxygen species (ROS) generation upon irradiation of photosensitizers in biological systems, photoexcitation of semiconducting photocatalysts in water/air purification processes or the activation of photoinitiators, the character and amount of the generated radicals brings crucial information on the ongoing processes.

Despite the emerging progress in the development and implementation of the advanced EPR techniques, the cw-EPR spin trapping remains a useful, yet tricky, tool to follow the presence and kinetics of the formation and decay of radicals in photochemical systems. In these applications a very cautious approach is inevitable, since not only the formation of the radicals, reflecting the behaviour of the studied system, but also their trapping by the spin trapping agent and the stability of so formed spin adduct is affected by numerous external factors (solvent, presence of oxygen, irradiation source). The experimental conditions have to be carefully considered in the interpretation of obtained data. On the other hand the specific choice of experimental system can expand the amount of

information obtainable from the method, e.g. due to the stabilization of radicals in selected solvents. High sensitivity of the EPR spectroscopy together with the fact that in spin trapping technique a spin trap molecule is added to the system which may affect not only the primary mechanism but also it may be the subject of photodegradation, consequently the radical species not directly involved in the photoinduced processes may be trapped. In our contribution the advantages and drawbacks of EPR spin trapping technique will be presented in the terms of its application in various photochemical systems using a variety of spin traps.

This work was supported by the Scientific Grant Agency of the Slovak Republic (Project VEGA 1/0026/18) and by the Slovak Research and Development Agency under the contract No. APVV-15-0053.



**Figure 1.** Experimental (–) and simulated (– –) EPR spectra (magnetic field sweep width; 12 mT) obtained upon 900 s UVA exposure of  $\text{TiO}_2$ /acetonitrile/ $\text{AgBF}_4$ /Ar suspensions containing 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) or 3,3,5,5-tetramethyl-1-pyrroline *N*-oxide (TMPO) spin trap.

## ESR: A Non-Invasive Technique for Quality Control in Carbon Fibre Production and the Characterisation of Carbon Fibre Products?

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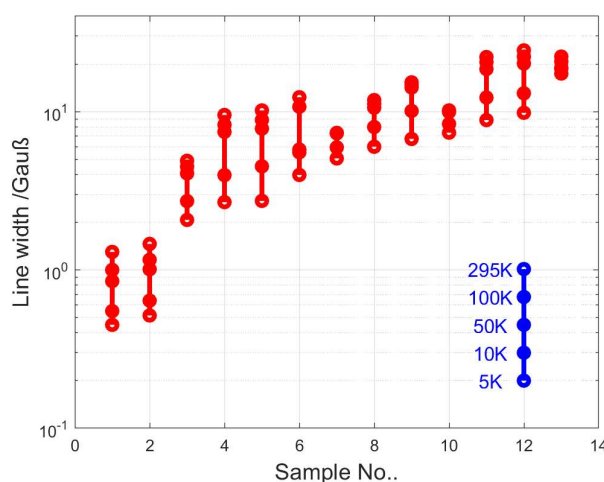
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Carbon fibres and materials based on carbon fibres are widely used in e.g. the construction of airplanes or cars due to the very high tensile strength and very low weight. Important elements in these fibres are more or less extended graphene like structures, elongated along the fibre direction by the carbonisation of pre-stretched polyacrylonitrile precursors.

Surprisingly, a wide range of these fibres exhibit rather strong ESR-signals (spin concentrations are up to  $\approx 10^{19}/\text{g}$ ). These lineshapes are practically perfect single Lorentzians with linewidths down to only 0.4 Gauß at low temperature ( $T = 4.2 \text{ K}$ ). These signals are due to paramagnetic centres at the edges of the graphene structures and the very narrow linewidths are due to strong exchange coupling via conduction electrons on the graphene.

This enabled us to use carbon fibres for double resonance experiments of the Overhauser shift type<sup>[1]</sup> and to establish them as high precision  $g$ -factor standards in ESR-spectroscopy.<sup>[2]</sup>

In this study we investigated 14 different fibre types from various manufactures, and the results for the linewidths are depicted in Figure 1. All fibres differ both in linewidth and in the change of the width as a function of temperature (4.2 K to 300 K). This allows to identify all the samples directly from their ESR-properties. We propose, that the ESR signals can be used as a “fingerprint” of the particular fibre type. There are correlations between the mechanical properties of these fibres (elasticity and strength) and the ESR-properties. In view of our experiments we suggest, that ESR can be used as a non-invasive technique for the characterisation of carbon fibres and carbon fibre based products, e.g. in quality control of the production process. The physics behind the strong narrowing of the ESR linewidth towards lower temperatures is due to the temperature dependence of the conduction electron mobility on the graphene like structures, enabling ESR to access the electron mobility and the temperature dependence of the mobility.



**Figure 1.** Line widths and range (bottom to top: 5 K, 10 K, 50 K, 100 K, 295 K) for 13 different carbon fibres.

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## Waterproofing Dynamical Decoupling: Nitroxides in H<sub>2</sub>O:Glycerol Glasses

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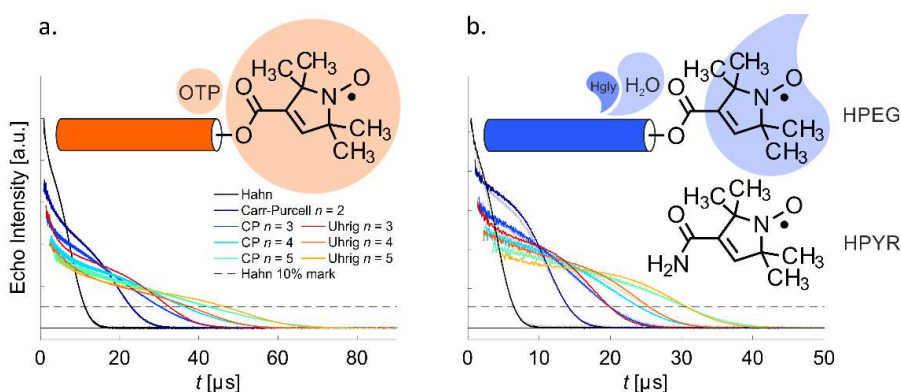
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We have previously shown under which conditions repeated refocusing best extends the phase memory times of nitroxides in *o*-terphenyl (OTP).<sup>[1]</sup> This being, low temperatures (*e.g.* 40 K) and concentration (*e.g.* 20  $\mu$ M) to freeze out relaxation inducing (intra)molecular motion and limit instantaneous diffusion, respectively. The best performing arrangement of  $n$   $\pi$  pulses (equidistant Carr-Purcell<sup>[2]</sup> vs. symmetric Uhrig<sup>[3]</sup>) depends on the matrix nature, as Uhrig outperforms CP in OTP (Figure 1a), while the opposite applies for deuterated OTP.

Here we go beyond the model character of OTP, and perform dynamical decoupling (DD) on nitroxides in water:glycerol glasses, bringing DD closer to EPR applications of chemical and biological interest. To this end, we introduce a water-soluble version of the rigid nitroxide, used in the OTP study, HPEG (Figure 1b). HPEG is best applicable in low  $\mu$ M concentration, as features in X-band CW spectra and Q-band DEER measurements proofed its tendency to aggregate.

We compare DD performance of the rigid nitroxides in OTP vs. water:glycerol, along with the analogous deuterated glasses, and find that some key features of DD are the same in both matrices. The relaxation behavior of HPEG matches the one of HPYR (Figure 1b) at 40 K, indicating that local motions in the glass voids do not significantly lead to dephasing. Results for our water soluble model compounds are representative for water-soluble spin-labelled proteins and peptides.



**Figure 1.** DD data set for  $n = 1$  to 5 recorded at 40 K for a) 20  $\mu$ M rigid nitroxide in OTP and b) 10  $\mu$ M HPEG (full colors) and HPYR (transparent colors) in water:glycerol 50:50 v/v. The dashed line marks 10% of the initial Hahn echo intensity and serves as a reference level.

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## Free Radical Formation in H<sub>2</sub>O<sub>2</sub>-Driven Iron Oxidation by Bacterioferritin

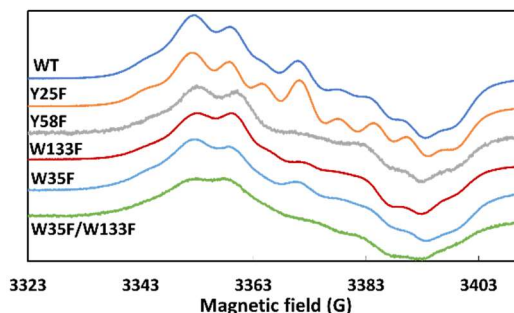
Jacob Pullin,<sup>1</sup> Justin M. Bradley,<sup>2</sup> Geoffrey R. Moore,<sup>2</sup> Michael T. Wilson,<sup>1</sup> Nick E. Le Brun<sup>2</sup> and Dimitri A. Svistunenko<sup>1</sup>

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Ferritins are an evolutionary response of biological systems to the toxicity and poor availability of free iron. Ferritins are made up of 24 subunits surrounding a hollow cavity, each subunit possessing a diiron ferroxidase centre: a catalytic site which plays a key role in iron oxidation and mineral core formation.<sup>[1]</sup> Bacterioferritin (BFR) is one of the ferritins encoded within the *E. coli* genome.

We have recently found that BFR is capable of oxidizing iron with H<sub>2</sub>O<sub>2</sub> several orders of magnitude faster than with O<sub>2</sub>. In this work, protein samples were deoxygenated, incubated with Fe<sup>2+</sup> and then mixed with a small aliquot of H<sub>2</sub>O<sub>2</sub> (all under argon) before being frozen in methanol cooled with dry ice. This yielded much higher intensity free radical EPR spectra than we reported before for oxygenated conditions. While iron loading of the oxygenated Y25F protein, in which the tyrosine implicated in iron oxidation is replaced, shows practically no free radical,<sup>[2]</sup> the H<sub>2</sub>O<sub>2</sub> treatment of the variant yields a radical of comparable intensity to the WT protein. By subtracting spectra measured at different microwave powers, or of different variants, it is possible to extract pure spectra of individual free radical species and make assignments that are testable by EPR spectral simulations.<sup>[3]</sup> In addition to an EPR lineshape previously assigned to Y25<sup>•</sup> in the oxygenated system, we propose formation of a tryptophanyl radical on W133 in two conformations. Anaerobic rapid freeze quench (RFQ) data show that free radical formation is on a comparable scale to a kinetic phase we have observed when monitoring Fe<sup>2+</sup> oxidation using stopped flow UV-vis spectroscopy.



**Figure 1.** The lineshapes of all recorded BFR mutant free radical EPR spectra, incubated with 48 Fe<sup>2+</sup>/24mer and then mixed with 250 μM H<sub>2</sub>O<sub>2</sub>, frozen after 10 s.

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## Triplet states of Donor-Acceptor Substituted Porphyrins

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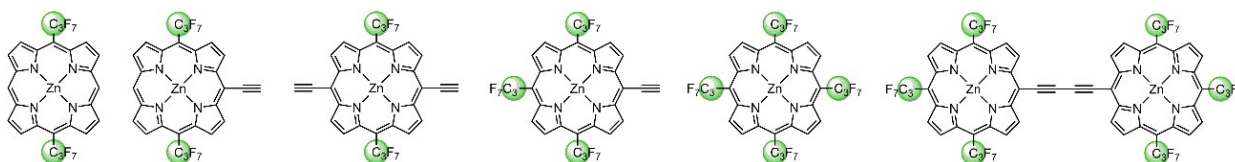
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<sup>3</sup> Institute of Physical Chemistry, University of Freiburg, Germany

The photoexcited triplet states of  $\pi$ -conjugated molecules are of interest in the fields of molecular electronics and photovoltaics.<sup>[1-3]</sup> Porphyrin oligomers composed of meso-meso linked units have been proposed as suitable building blocks for molecular wires in nano-scale devices.<sup>[1-3]</sup> Controlling the electron delocalization is important for mediating the efficiency of electronic communication between sub-units and there is currently no comprehensive model which relates the structure to the delocalization.

Transient EPR spectroscopy in combination with pulse electron nuclear double resonance (ENDOR) has previously been employed to characterise the photo-generated triplet states of linear and cyclic zinc porphyrin oligomers.<sup>[4]</sup> Studies have also explored the influence of the bridging linker,<sup>[5]</sup> where varying the length or geometry of the meso-meso linker imposes constraints on the dihedral angles between adjacent porphyrin rings. In addition, the significance of symmetry was explored by altering the distribution of side groups in porphyrin oligomers thus rendering the porphyrin units inequivalent; this work demonstrated how the symmetry of the porphyrin system affects the triplet state delocalization.<sup>[6]</sup>

In this work, we consider the photo-generated triplet states of a series of linear zinc porphyrin systems containing monomers with acceptor groups and oligomers with donor and acceptor groups in the meso position. Transient, magnetophotoselection and pulse ENDOR spectroscopies are exploited to gain a better understanding of Zero Field Splitting and Hyperfine Coupling parameters, all of which ultimately depend on the shape and distribution of the triplet spin density. Preliminary results have so far provided information into how different combinations of acceptor-donor groups influence the triplet state wavefunction. Our current focus is concerned with reconciling the experimental data with DFT calculations and developing simulation routines to interpret the results of a magnetophotoselection experiment.



**Figure 1.** Subset of the investigated molecular structures

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## An Investigation of Refocused Out of Phase DEER and RIDME

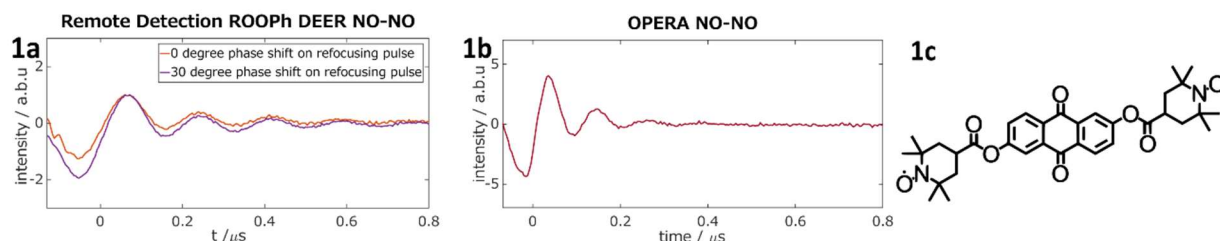
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Pulsed EPR dipolar spectroscopy is an important family of techniques used to measure interactions on a nanometre length scale for structural determination. Many methods exist including **Relaxation Induced Dipolar Modulation Enhancement** (RIDME) and **Double Electron Electron Resonance** (DEER).<sup>[1–3]</sup> Modified forms of these techniques have been published such as increased modulation depth and trace length variants developed to improve the quality of recorded data.<sup>[4,5]</sup> Both RIDME and DEER traces include a modulated dipolar component and an unmodulated background. Methods have also recently been developed for DEER to allow the unmodulated component of the data to be minimised by using the out of phase component. This was initially achieved by measuring the DEER signal in the presence of a large magnetic field (above 6 T) and at low temperature (below 5 K). Here the polarisation of the spin levels results in a measurable out-of-phase component of the DEER signal.<sup>[6]</sup> More recently, **Refocused Out Of Phase** (ROOPh) DEER was published, where in an additional group of pulses is used to remove the in phase and refocus the out of phase component of the signal.<sup>[7]</sup>

In this work we build on the published ROOPh DEER methodology, implementing both direct detection and remote detection schemes. It was found that, for the remote detection scheme a phase shift of 30° on the refocusing pulses relative to the first pulse resulted in improved signal to noise. We investigated this by testing different phases of the refocusing pulses. The phase shift is most likely to be a dynamic phase shift resulting from the first pump pulse (**1a**).<sup>[8]</sup> We also apply the same principles to the RIDME experiment, developing a new pulse sequence; **Out of Phase Experiment RIDME Application** (OPERA). This has been successfully shown to filter the unmodulated component of the RIDME signal and refocus the out-of-phase component of the signal (**1b**) for a model nitroxide bi-radical (**1c**).



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## High Field Orientationally Selective Multi-Spin PELDOR – What is going on?

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In this presentation, a number of anomalous effects are examined, associated with W-band, orientationally-selective, PELDOR measurements on a heptameric mechano-sensitive ion channel protein. In this system we often see very strong sensitivity gains from W-band measurements compared to X-band measurements. We have observed strong saturation of echo signals in the centre of the spectrum, and echo signals that become increasingly larger with increasing selectivity of the exciting pulse. This does not appear to be dependent on sample concentration, nor sample aggregation. The mechanism thus looks to be dependent on strong intramolecular instantaneous diffusion, and this mechanism also appears to be at least partially consistent with relaxation data. However, it is then becomes very difficult to make any quantitative model fit the experimental data, as so few spins are involved in this process. For certain samples, the strongest PELDOR oscillations are also observed when high  $B_1$  field pump and probe pulses are placed at the very edges of the spectrum, when the probability of exciting no more than one spin with either pump or probe is high. In some systems these give anomalously narrow distance distributions that are nevertheless entirely consistent with the expected configuration. However, when multiple spins are excited in the centre of the line then the modulation depth becomes much smaller than expected, and distance distributions are observed to be much broader. These observed modulation depths cannot be accounted for using standard power scaling nor by orientational effects. We also observe PELDOR signals that have a dependence on sequence length in ways that are not easily accounted for by explanations that have previously appeared in the literature. There thus appears to be something missing from the conventional description of multi-spin PELDOR, at least on relatively large multi-spin systems. In this presentation we examine a number of mechanisms that might account for these effects.



**Figure 1.** HIPER W-band spectrometer used to measure orientational selective PELDOR on a heptameric mechano-sensitive ion channel protein.

## Magnetic-Field-Tuned Phase Transition of a Copper Compound from the Isolated-Spin to the Coupled-Spin Regime Probed by EPR

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Molecular compounds with one or more coordinated metal ions per molecule may be connected by covalent or non-covalent paths to their neighbours. These so-called coordination polymers are relevant to several fields such as molecular magnetism, catalysis, biochemistry, and others. Besides, they may display interesting phenomena such as quantum phase transitions. We report electron paramagnetic resonance (EPR) studies at Q- and X-band of powder and oriented single crystals of [Cu(N,N-dimethyl-N'-benzoylthiourea)(2,2'-bipyridine)Cl], called CuBMB.<sup>[1]</sup> Single crystal EPR spectra at Q-band and room temperature display abrupt mergings and narrowing of the peaks arising from two rotated copper sites with the orientation of an external magnetic field  $B_0$ . Weak intermolecular exchange interactions  $|J_i|$  between neighbour copper spins, responsible for the exchange narrowing processes produce a quantum transition from an array of quasi-isolated spins to a quantum-entangled spin array. This transition occurs when the magnitudes of the anisotropic contributions to the Zeeman couplings, tuned with the direction of  $B_0$ , approach these  $|J_i|$  and produce level crossings. We pinpoint the excellent capability of EPR in this kind of studies, where weak exchange coupling magnitudes would require extremely low temperatures to be detected via thermodynamic techniques such magnetic susceptibility measurements. The effect of an entangled phase in the EPR spectrum directly affects the properties of an absorption profile via the modulation of the linewidth by the exchange narrowing phenomenon even at room temperature. Besides, we indicate specific features in the powder spectra that point to the presence of an entangled phase. A similar approach can be followed for any system where either inter or intra molecular exchange coupling causes the collapse of the EPR spectra around transition crossings.<sup>[2]</sup> In conclusion, it is clear that molecules can be engineered to behave according to the expected phase depending on the application and we intend to further investigate this phenomenon at higher frequencies and magnetic fields for a wider range of materials and spin-spin interaction magnitudes.

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## Spectroscopy of High-Spin Co(II) Single-Molecule Magnet

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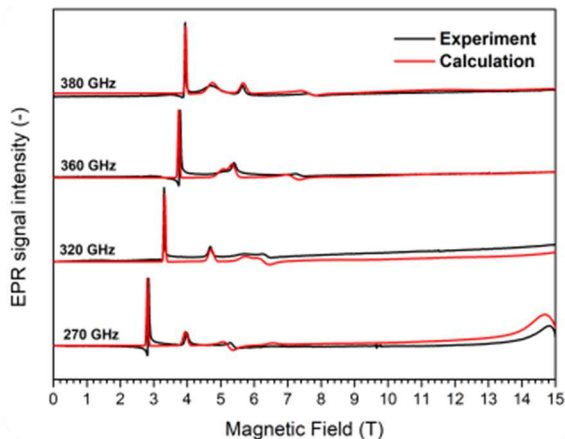
<sup>2</sup> Department of Chemistry, University of Florence, Italy

Novel approaches to electronics are based on two disciplines: spin electronics (spintronics) and molecular electronics. A fundamental connection between these two fields can be established using single-molecule magnets (SMMs).<sup>[1]</sup> Herein, we report on a complex spectroscopic investigation of selected SMM by high-frequency electron paramagnetic resonance (HF-EPR), ultraviolet-visible (UV-VIS), and X-ray photoelectron (XPS).

Bulk properties of cobalt-ferrocene dimer (CFD) with linear chemical formula:  $[X_2Co(P(C_6H_5)_2C_5H_4)_2Fe]$ , where  $X = Br$ , and  $(P(C_6H_5)_2C_5H_4)_2Fe = dppf$ , were investigated by HF-EPR and allowed us to determine that the  $Co^{2+}$  ions are in the high-spin state (i.e.  $S = 3/2$ ) with spin Hamiltonian parameters:  $g_x = 2.22$ ,  $g_y = 2.22$ ,  $g_z = 2.28$  and

zero-field splitting terms:  $D = -11.2 \text{ cm}^{-1}$  and  $E/D = 0.09$ , representing suitable bulk magnetic properties for applications as SMMs.<sup>[2]</sup> We also performed UV-VIS and XPS measurements on both bulk and nanostructured CFD. XPS qualitative and quantitative analyses were used to evaluate reference samples consisting of bulk (dppf) and  $Co(dppf)Br_2$ . We investigated two batches of samples, first from sublimation in UHV-deposition chamber, second from drop-cast in nitrogen atmosphere.

In conclusion, we found out that it is possible to prepare thin films of intact CFD by drop-cast in nitrogen atmosphere and evaporation by carefully selecting an appropriate preparation environment and specific solvent in the case of wet-chemistry based methods and by controlling sublimation temperature in the case of the UHV-based evaporation.



**Figure 1.** HF-EPR spectra of  $Co(dppf)Br_2$  for four frequencies at 5 K.

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# Electron Paramagnetic Resonance of Fe<sup>3+</sup> in BaTiO<sub>3</sub>

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Barium titanate is ferroelectric and exhibits a high room temperature dielectric constant. It has a Curie temperature of 393 K, transforming from a cubic (Pm3m) to a tetragonal structure (P4mm). On cooling two further structural phase transitions occur, at approximately 273 K to an orthorhombic (Amm2) phase, then to a rhombohedral (R3mR) phase at approximately 200 K. All phase transitions are first order. Iron is a ubiquitous substitutional impurity in BaTiO<sub>3</sub>, and was first detected by EPR in 1954.<sup>[1]</sup>

Interest in BaTiO<sub>3</sub> has revived in recent due to efforts to discover new Pb-free piezoelectric materials, for example solid solutions of Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> with BaTiO<sub>3</sub>. Iron doped compositions are expected to exhibit improved piezoelectric properties resulting from ferroelectric domain pinning by dipole defects.<sup>[2]</sup> The aim of this preliminary EPR study was to investigate and confirm the spin-Hamiltonian (SH) parameters for Fe<sup>3+</sup> in tetragonal phase,<sup>[3]</sup> and orthorhombic phase,<sup>[4]</sup> BaTiO<sub>3</sub>. Measurements were performed on a nominally undoped BaTiO<sub>3</sub> crystals grown at Argonne National Laboratory and on a Fe-doped crystal supplied by Technische Universität Darmstadt at 9.5 GHz using a Bruker EMX spectrometer. Line position ‘roadmaps’ were measured as a function of angle from (100) oriented crystals at room temperature (Figure 1), 200 K (Figure 2) and 213 K.

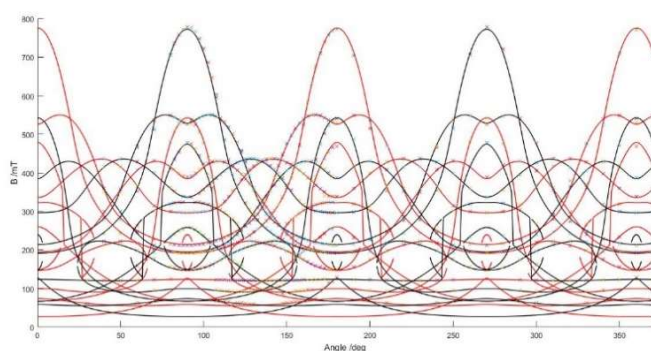


Figure 1. 300 K Fe<sup>3+</sup> roadmap

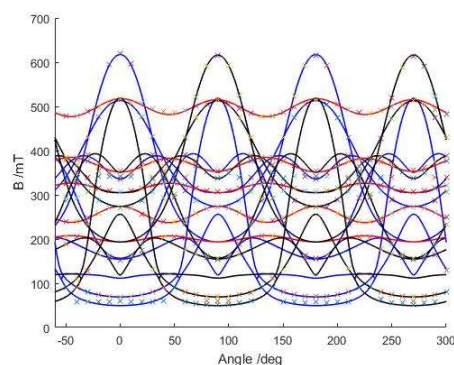


Figure 2. 200 K Fe<sup>3+</sup> roadmap

The line position roadmaps were fitted using  $\hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{S}} + \sum_{n=2,4} B_n^m \hat{O}_n^m$ , where  $\hat{O}_n^m$  are the conventional

Stevens operators. The resulting SH parameters were found to be in good agreement with previous work. It was not possible to determine an accurate non-zero value for the orthorhombic term,  $B_2^2$ , for measurements in the orthorhombic phase.

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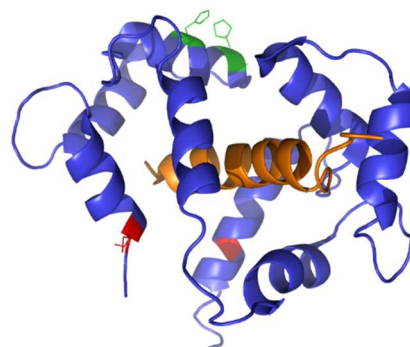
## Conformational Changes in the Structure of Human Calmodulin in a Calcium-Substrate Dependent Manner

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Human Calmodulin 1 is a protein ubiquitously expressed within all tissue in the human body. The protein itself provides a suitable target for refinement of in-cell EPR methodology due to the amount of structural information already available as well as the different cellular pathways it is involved in. By understanding the range of function through conformational changes that are possible, the proteins that Calmodulin interacts with may be targeted or inhibited for the purposes of disease mediation and/or treatment.

For this research, a mutant protein consisting of Human Calmodulin 1 (CaM1) and the calmodulin-binding domain of skeletal muscle myosin light chain kinase (skMLCK) has been synthesised to produce CaM1-M13 (PDB: 2BBM) shown in Figure 1. This is to ensure the protein can be measured locked around a substrate and compared with Calmodulin in an open State as based on research carried out by Ikura *et al.*<sup>[1]</sup> To this end, two cysteines have been substituted into the structure as well as a second histidine i4 of an existing histidine.



**Figure 1.** CaM1-M13 complex in presence of calcium. M13 alpha helix highlighted in orange. Both aa10 and aa146 cysteines below the M13 section are represented in red. The natural aa107 and substituted aa111 histidines above M13 are green. The three labelling regions surround the M13 alpha helix in a triangular formation when CaM1 is bound to M13 in the presence of calcium.

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## Pulsed EPR Investigation of Metal Binding to Coiled-Coil Peptides

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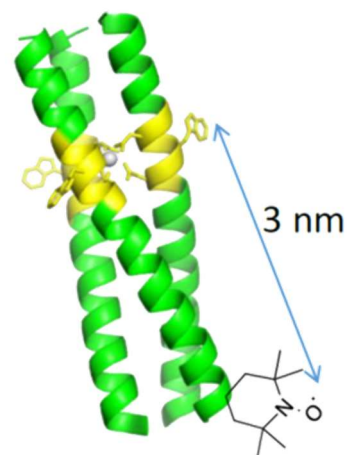
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A peptide coiled-coil was developed de novo as a potential medical contrast agent for Magnetic Resonance Imaging (MRI). The coiled-coil is composed of three alpha helices intertwined, containing a metal binding site.<sup>[1,2]</sup>

The site was designed to bind Gadolinium ions. Gd(III) complexes have been employed as MRI contrast agents for many years and more recently as spin labels in EPR.<sup>[3]</sup> The latter due to Gadolinium's high spin nature and relaxation properties, which has spurred the development and refinement of Gd(III) for labelling purposes.<sup>[4]</sup> However, this presentation will focus on determining, by EPR, whether these peptides bind to metals other than Gd(III) e.g. Cu(II).

We shall present a metal-binding coiled-coil with a TOAC (nitroxide) spin label introduced at its terminus. Relaxation studies, DEER and RIDME have been used to probe for structural information between the metal centre and TOAC label with regards to metal-peptide binding.



**Figure 1.** MD Simulation of the single metal binding MB1-2 coiled-coil structure showing the binding site for the introduced metal.<sup>[1]</sup> TOAC has been drawn to illustrate the expected distance between the metal binding site and the nitroxide.

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## EPR Characterisation of Trityl Radicals with the Finland Trityl Radical Scaffold and Two Orthogonal Functional Groups

Agathe Vanas,<sup>1</sup> Henrik Hintz,<sup>2</sup> Daniel Klose,<sup>1</sup> Gunnar Jeschke<sup>1</sup> and Adelheid Godt<sup>2</sup>

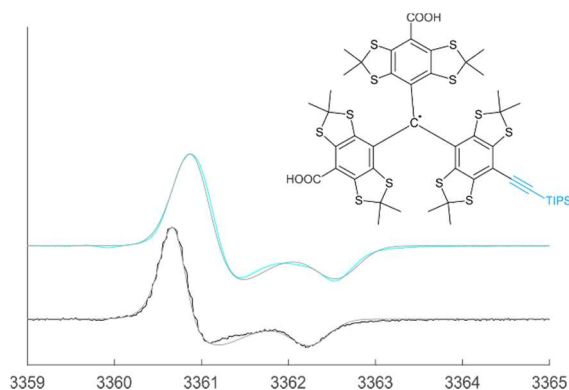
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<sup>2</sup> Faculty of Chemistry and Center for Molecular Materials (CM<sub>2</sub>), Bielefeld University, Universitätsstrasse 25, 33615 Bielefeld, Germany

Trityl radicals are carbon centred radicals of which Finland Trityl Radical (FTR) became popular in EPR applications. In recent years, FTR based spin labels were derived and used for distance measurements.<sup>[1]</sup> The central advantages of trityl radicals lie in their reduction resistance and long relaxation times, which make distance measurements feasible in cells as well as at non cryogenic temperatures.<sup>[1,2]</sup>

FTR possesses three chemically identical carboxyl groups. For many applications, especially for application as a spin label, only one of them should be functionalized. This is usually achieved via a statistical reaction giving a mixture of 1-, 2- and 3-fold modified FTR which very often requires a quite challenging separation and results in low yields. To avoid such a statistical modification, we developed an approach in which the FTR scaffold is assembled through addition of an aryllithium with one type of substituent to a diarylketone with another type of substituent. On this route, two FTR-type trityl radicals carrying the chemically orthogonal groups, carboxyl and triisopropylsilylethynyl were synthesized.<sup>[3]</sup>

We characterised the two FTR-type trityl radicals using continuous wave and pulse EPR spectroscopy at X-band and W-band frequencies and compared their spectroscopic properties to FTR. Longitudinal and transverse relaxation behaviour were studied at both fields at a temperature of 50 K. Furthermore, spectral properties of the trityl radicals were investigated in both frequency bands and g-anisotropies were determined through fitting of W-band spectra. The obtained data show that one or two carboxyl groups of FTR can be substituted for ethynyl groups without significantly altering the most important spectroscopic properties of FTR. Hence, we deem these variants promising candidates for the ongoing design of trityl spin labels.



**Figure 1.** FTR (black) and the modified structure (blue) with the functional groups triisopropylsilyl (TIPS) and carboxyl are shown as structures along with their W-band cw EPR spectra.

[1] O. Krumkacheva and E. Bagryanskaya, in *Electron Paramagnetic Resonance*, ed. V. Chechik and D. M. Murphy, The Royal Society of Chemistry, Cambridge, UK, 2017, vol. 25, p. 35.

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# CHirped, ORdered Pulses for ULtra-Broadband [ESR] Spectroscopy

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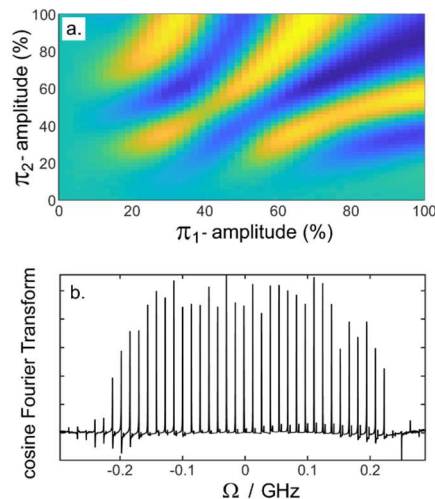
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For measurements of bulk samples in magnetic resonance, the inhomogeneity of RF (MHz, GHz) magnetic field strength impacts uniform phase rotation of spins at frequencies offset from the transmitter. Prior development of CHirped, ORdered pulses for Ultra-broadband Spectroscopy (CHORUS) for NMR has allowed nearly perfect phase uniformity at a large range of offsets and insensitivity to B1 inhomogeneity by virtue of a second  $\pi$  pulse used to achieve the echo or FID. Such methods are applicable to heteronuclei such as  $^{19}\text{F}$ , with a wide range of chemical shifts.<sup>[1,2]</sup>

In the present work focussed on ESR spectroscopy, we compare the phase uniformity as a function of linear chirp and WURST pulses, each as  $\pi/2$  pulses and as two-pulse echoes, with an improved version of the CHORUS sequence.<sup>[3]</sup> A sample of single point x-lithium phthalocyanine has a FWHM linewidth of 200 kHz, allowing probe of the excitation profile in parallel to NMR experiments. Use of the Bruker EleXSys II SpinJet and MS2 resonator provides largely unperturbed excitation in excess of 500

MHz, while field stepping is used in the place of the convenient digital control of transmitter and receiver frequencies found in NMR spectrometers.

It is well known that the two-pulse chirp and WURST echoes both enable a degree of phase uniformity, however, the use of the CHORUS sequence improves on those characteristics by employing two  $\pi$  pulses. By shifting the microwave carrier frequency to less favourable values that encompass a variation of more than two in B1-max within the excitation bandwidth, all pulse sequences are of reduced efficacy. Resonator transfer functions are considered by both microwave nutation and 0.5 ns impulse response. Application improvements by the phase uniformity and B1 insensitivity are possible with other pulses characterized by uniform rotations performed in concert with the CHORUS sequence.



**Figure 1.** Pulse optimization of  $\pi$ -pulses for on-resonant FID, panel a, and b, projection offsets in 64–160–128 ns CHORUS pulses.

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[3] M. Foroozandeh, M. Nilsson and G. A. Morris, submitted.

## Optically-induced Dynamical Nuclear Polarization in Diamond Materials

Rémi Blinder,<sup>1</sup> Yuliya Mindarava,<sup>1</sup> Jochen Scheuer,<sup>1</sup> Tobias Speidel,<sup>2</sup> Christian Laube,<sup>3</sup> Viatcheslav N. Agafonov,<sup>4</sup> Valery A. Davydov,<sup>5</sup> Volker Rashe<sup>2,6</sup> and Fedor Jelezko<sup>1</sup>

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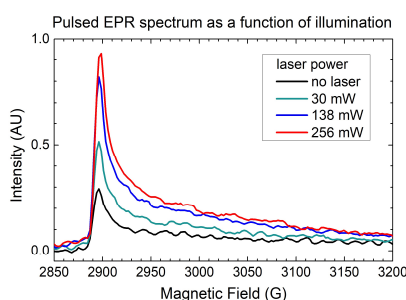
<sup>4</sup> François Rabelais, University of Tours, Tours, France

<sup>5</sup> L.F. Vereshchagin Institute for High Pressure of the RAS, Troitsk, Russia

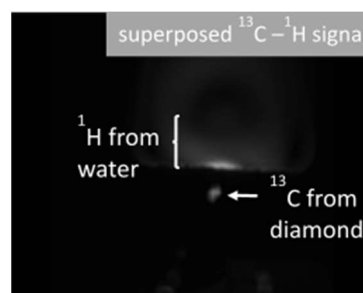
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Magnetic Resonance Imaging (MRI) is a widely used technique for medical diagnostic, and as a tool for life sciences in general. Though it enables to perform high contrast imaging, certain applications, such as  $^{13}\text{C}$  MRI for imaging of metabolic/enzymatic conversion processes, which would be useful for cancer detection, suffer from a low sensitivity. In the recent years, various techniques have been explored in order to improve the sensitivity, which is achieved most often by enhancing the nuclear spin polarization above the thermal value. One of these techniques, called Dynamical Nuclear Polarization (DNP), relies on the transfer of polarization from electron spin to the nuclei. Diamond is a promising material for DNP, since higher polarization values can theoretically be reached by targeting the negatively charged Nitrogen Vacancy defect ( $\text{NV}^-$ ) with light irradiation, and then transferring its polarization to the surrounding  $^{13}\text{C}$  nuclei, which is achieved with microwave irradiation.

We present new results concerning the hyperpolarization of  $^{13}\text{C}$  in bulk diamond crystals, as well as the characterization of NMR and EPR properties of powders (particle size in the 10 nm – 10  $\mu\text{m}$  range). In NMR, we measured the nuclear  $T_1$  time of such powders with either natural abundance of  $^{13}\text{C}$  or, up to 30%  $^{13}\text{C}$ -enriched, under both static and Magic Angle Spinning conditions. The enhancement of  $\text{NV}^-$  polarization under laser irradiation, which is a prerequisite for hyperpolarization, has been observed in a pulsed EPR experiment (Figure 1). Finally, as a proof of concept for future imaging experiments, we report the hyperpolarization of a bulk diamond crystal and its observation in a high-field 11.7 T preclinical MR system (Figure 2).



**Figure 3.** Field-swept ESE-detected spectrum, acquired in X-band EPR, of the low field most intensive  $\text{NV}^-$  line in diamond powder, with: no light irradiation (black), and under various intensities of green laser illumination (other colors), enhancing the polarization of  $\text{NV}^-$  centers.



**Figure 3.** Image of a hyperpolarized diamond crystal in a high-field 11.7 T preclinical MR system. The  $^{13}\text{C}$  signal (from the diamond) is here overlaid with the thermal signal from  $^1\text{H}$  in an adjacent water phantom. Diamond sample size is 5×4×2 mm.

**2020**

The 53<sup>rd</sup> Annual International Meeting  
*of the*  
ESR Spectroscopy Group  
*of the*  
Royal Society of Chemistry



Chancellors Hotel

The University *of* Manchester

Sunday 29<sup>th</sup> March – Thursday 2<sup>nd</sup> April

Sunday 7 <sup>th</sup> April	Monday 8 <sup>th</sup> April	Tuesday 9 <sup>th</sup> April	Wednesday 10 <sup>th</sup> April	Thursday 11 <sup>th</sup> April
	09:00 Welcome	Chair Kuprov 09:00 Goovaerts 09:40 Fábregas Ibáñez 10:00 Oganessian 10:20 Mathies	Chair Timmel 09:00 Di Valentín 09:40 Tait 10:00 Willi 10:20 Galazzo	Chair Keeble 09:00 Norman 09:40 Haywood 10:00 Wedge 10:20 Lovett
	10:30 Coffee break	10:40 Coffee break	10:40 Coffee break	10:40 Coffee break
	Chair Goovaerts 11:00 Yulikov 11:30 Concilio 11:50 Kacprzak	Chair Schiemann 11:10 Ruthstein 11:40 Fittipaldi 12:00 Ionita 12:20 Azarkh	Chair Norman 11:10 Lurie 11:40 Pliotas 12:00 Cogdell	Chair McInnes 11:05 ScotCHEM 11:10 Chilton 11:40 Weiss 12:00 Bode 12:20 Zalibera
	12:10 IES Laudatio 12:20 IES Silver Medal Robert Bittl		12:30 Lunch	12:40 Conference close
	12:40 Lunch	12:40 Lunch	Chair Collison 14:00 EPSRC EPR Service 14:05 Bowen 14:35 Hageleuken 14:55 Kuprov 15:15 Svistunenko	12:45 Lunch
15:00 Registration	Chair Bode 14:10 Elpelt 14:30 Breitgoff 14:50 Šiménas 15:10 Kuzhelev	14:10 Free Afternoon  Distillery tour: 15:00 – 17:00  National EPR Service Steering Committee Meeting  ESR Committee Meeting	15:35 Coffee break	
	15:30 Coffee break		16:05 Poster Session 2	
	16:00 Poster Session 1	17:30 ESR Group AGM	Chair Sproules 17:15 Lombardi 17:25 McGuire 17:35 Esteban Hofer 17:45 Moise	
	Chair Bowen 17:10 Erlenbach 17:30 Chabbra 17:50 Teucher 18:10 Ritsch	18:30 Dinner	18:00 Bruker Thesis Laudatio 18:10 Bruker Thesis Lecture Claire Motion	
18:30 Dinner	19:00 Dinner	20:00 Bruker Prize Laudatio 20:10 Bruker Prize Lecture Marina Bennati		
20:30 Welcome Reception	21:00 JEOL Reception	21:00 Bruker Reception	19:30 Banquet & Ceilidh	