The 45th Annual International Meeting

of the

ESR Spectroscopy Group

of the

Royal Society of Chemistry

The University of Manchester

25th – 29th March 2012

Contents

Conference Programme

Sunday 25th March		
16.00 – 18.30	Registration	Chancellors Reception
18.30 – 20.00	Dinner	Chancellors Carriage Restaurant
20.00 – 22.30	RSC Wine Reception and free bar	Chancellors Conservatory and bar

Monday 26th March		
07.30 – 08.55	Breakfast	Chancellors or Luther King House or Willowbank Hotel
Session 1 Chair: David Collison		
08.55 – 09.00	Mark Newton	Conference opening and welcome note
09.00 – 09.30	Richard Winpenny	**Keynote Lecture:** EPR Studies of Rings and Dimers of Rings
09.35 – 09.50	Irina Drozdyuk	Intercluster exchange interactions and spin state switching in copper nitroxide based molecular magnets $Cu(hfac)_2LR$ studied by EPR
09.55 – 10.10	Shigeaki Nakazawa	Quantum operations by pulsed ESR spectroscopy: Molecular design for biradical and triradical qubits
10.15 – 10.30	Petra Lüders	Relaxation Enhancement in Orthogonal Spin Pairs – Precision and Short Distance Limitation –
10.35 – 11.05	Tea & Coffee	Chancellors Conservatory
Session 2 Chair: Ilya Kuprov		
11.05 – 11.25	Gavin Morley	**Invited Lecture**: Quantum control of hybrid nuclear-electronic qubits
11.30 – 11.45	David Keeble	EPR of Fe^{3+} centres in $SrTiO_3$: Monodomain crystals to thin films
11.50 – 12.05	Vasile Nistor	Spying with Mn^{2+} ions the structure changes during the thermal decomposition of $Zn_5(CO_3)_2(OH)_6$ and $Zn(OH)_2$ into nanostructured ZnO
12.10 – 12.25	Mario Chiesa	Elucidating the Nature and Reactivity of Metal Ions Incorporated in the Framework of Aluminophosphate Molecular Sieves. New Evidences from HYSCORE and Pulse-ENDOR Spectroscopy
12.30 – 14.00	Lunch	Chancellors Conservatory
Session 3 Chair: Fraser MacMillan		
14.00 – 14.15	Alice Bowen	**Jeol Student Prize Talk:** Utilizing the TWT linear region: Double Electron-Electron Resonance (DEER) with multiple excitation pulses and dead-time free three-pulse DEER
14.20 – 14.35	Ilia Kaminker	**Jeol Student Prize Talk:** A novel triple resonance correlation sequence for Resolving and Assigning Signals in ELDOR-Detected NMR Spectra
14.40 – 14.55	Tomasz Mazur	**Jeol Student Prize Talk:** EPR/HYSCORE and DFT study of nickel adducts with O_2, CO and NO molecules encaged in zeolites
15:00 – 15:15	Christoph Meier	**Jeol Student Prize Talk:** Microcrystalline Silicon: Orientation dependence of light induced EDMR signals
15:20 – 15:35	Gunnar W. Reginsson	**Jeol Student Prize Talk:** Trityl: A new spin label for nanometer distance measurements
15.40 – 17.00	Tea & Coffee: **Posters (EVEN)**	Chancellors Conservatory

Session 4 Chair: Victor Chechik		
17.00 – 17.25	Arzhang Ardavan	**Invited Lecture**: Quantum information processing with molecular nanomagnets
17.30 – 17.45	Simon Bennie	Electronic and Magnetic Properties of a Tris(hydroxo) bridged Chromium dimer, A challenge for DFT
17.50 – 18.05	Johannes McKay	New techniques in determining the spin label orientation using high power W-Band PELDOR
19.00 – 20.30	Dinner	Chancellors Carriage Restaurant
20.30 – 24.00	JEOL Reception and free bar	Chancellors Conservatory and Bar

Tuesday 27th March		
07.30 – 09.00	Breakfast	Chancellors or Luther King House or Willowbank Hotel
Session 5 Chair: Christiane Timmel		
09.00 – 09.30	Walter Kockenberger	**Keynote Lecture:** From electron-nuclear spin pairs to the electron spin interaction with the bulk nuclei: A closer look at dynamic nuclear polarisation
09.35 – 09.50	Graham Smith	Techniques to improve sensitivity and capability in high field pulsed EMR experiments
09.55 – 10.10	Wei Wu	Theoretical modelling of orientation-dependent EPR spectra in organic solar cells
10.15 – 10.30	Ilya Kuprov	Closing the simulation loop: direct fitting of atomic coordinates of radicals to experimental ESR data
10.35 – 11.05	Tea & Coffee	Chancellors Conservatory Group photograph of delegates
Session 6 Chair: Damien Murphy		
11.05 – 11.25	Georg Gescheidt	**Invited Lecture:** Probing (Anti)-oxidative effects with time-resolved EPR and CIDNP
11.30 – 11.45	René Boeré	ESR and Electrochemistry Studies on Sterically Congested R_3E (E=As,P) and R_2PPR_2
11.50 – 12.05	Goetz Bucher	Naphthoxanthenyl: An Unusually Stable Carbon-Centered Free Radical
12.10 – 12.25	Jeffrey Harmer	Electron delocalization in multi-porphyrin systems probed by EPR
12.30 – 12.45	Dimitri Svistunenko	Dehaloperoxidase – a Tyrosine Radical Juggler
12.50 – 14.00	Lunch	Chancellors Conservatory
14.00 – 18.00	Free afternoon: opportunity to visit Manchester attractions, *e.g.* Museum of Science and Industry or other cultural assets – see info leaflets in delegate pack.	Frequent buses into Manchester city centre from Wilmslow Road. See separate map in folder for details of bus routes and location of attractions. To get to Museum of Science and Industry or the Imperial War Museum North, it may be easier to share a Taxi there and back.
18.00 – 19.30	Dinner	Chancellors Carriage Restaurant
Session 7 Chair: Mark Newton		
19.30 – 21.00	Kev Salikhov	**Bruker Lecture:** Quantum computing on electron spins using the pulse EPR spectroscopy methodology
21.00 – 24.00	Bruker Reception and free bar	Chancellors Conservatory and Bar

Wednesday 28th March		
07.30 – 09.00	Breakfast	Chancellors or Luther King House or Willowbank Hotel
Session 8 Chair: David Norman		
09.00 – 09.30	Heinz-Juergen Steinhoff	**Keynote Lecture:** Structure and Conformational Dynamics of Nucleic Acids and Membrane Protein Complexes Studied by Site-Directed Spin Labeling
09.35 – 09.50	Chris Kay	Investigation of IKK Structure and Activation by site-directed spin labeling and EPR Spectroscopy
09.55 – 10.10	Elena Gabriela Ionita	Investigating cyclodextrin/ PEG hydrogels properties with spin probes
10.15 – 10.30	Alistair Fielding	Multifrequency Electron Paramagnetic Resonance Characterization of PpoA, a CYP450 Fusion Protein that Catalyses Fatty Acid Dioxygenation
10.35 – 11.05	Tea & Coffee	Chancellors Conservatory
Session 9 Chair: Graham Smith		
11.05 – 11.25	Steffen Glaser	**Invited Lecture**: Optimal Control of Spin Dynamics in Magnetic Resonance
11.30 – 11.45	Gunnar Jeschke	Characterization of protein conformational changes with sparse spin label distance constraints
11.50 – 12.05	Bela Bode	PELDOR in membrane proteins: potential pitfalls and loopholes
12.10 – 12.25	Janet Lovett	DEERS – combining the sensitivity of 3p-DEER with the versatility of 4p-DEER
12.30 – 14.00	Lunch	Chancellors Conservatory
Session 10 Chair: Dima Svistunenko		
14.00 – 14.15	David Norman	Using very long distance and orientation measurement to elucidate the structure of the histone Chaperone Vps75
14.20 – 14.35	Katharina Pirker	Investigation of the intermediate state of the chaperone usher pathway in Type 1 *E. coli* using SDSL-EPR
14.40 – 14.55	Dennis Kurzbach	Assessing the Solution Shape and Size of Charged Dendronized Polymers Using Double Electron Electron Resonance
15.00 – 15.15	Claire Motion	Composite Pulses in W-band PELDOR experiments
15.20 – 16.40	Tea & Coffee: **Posters (ODDS)**	Chancellors Conservatory
Session 11 Chair: Chris Kay		
16.40 – 17.00	Christiane Timmel	**Invited Lecture:** A multifrequency approach: using RF and microwave fields to unravel the recombination kinetics of a photoinduced radical pair
17.05 – 17.20	Marilena Di Valentin	Insight into the Electronic Structure of the Carotenoid Triplet state in Photosynthetic Proteins revealed by ESEEM and Pulse ENDOR
17.25 – 17.40	Fraser MacMillan	EPR accessibility measurements of P-glycoprotein show topography of TM6/TM12 region in different conformational states
17.45 – 18.00	Johann Klare	Structure and Function of the Sodium/Proline Transporter PutP studied by EPR Spectroscopy
18.05 – 18.35	AGM RSC ESR Spectroscopy Group	Flowers Lecture Theatre (all welcome to attend)
19.30 – 22.30	Banquet	Woolton Hall (short walk from Chancellors)

Thursday 29th March		
07.30 – 09.00	Breakfast	Chancellors or Luther King House or Willowbank Hotel
Session 12 Chair: Eric McInnes		
09.00 – 09.30	Takeji Takui	**Keynote Lecture:** New aspects of nitroxides and open-shell graphene fragments chemistry: From quantum computers to energy conversion elements
09.35 – 9.50	Alena Nishchenko	EPR study of the mobility of nitroxide radicals confined in MIL-53(Al) nanochannel system
9.55 – 10.10	Mariana Stefan	Multifrequency EPR of Mn^{2+} in II-VI semiconductor nanocrystals
10.15 – 10.45	Tea & Coffee	Chancellors Conservatory
Session 13 Chair: Mark Newton		
10.45 – 11.05	Robert Bittl	**Invited Lecture**: EPR in bioenergetics and photovoltaic research
11.10 – 11.25	Maxie Roessler	Nature of the Fe-N bond in the reversibly superoxidized proximal [4Fe-3S] cluster of O_2-tolerant [NiFe]-hydrogenases as revealed by HYSCORE
11.30 – 11.45	Till Biskup	Cryptochromes: Potential compass molecules with an unexpected variety of electron transfer pathways
11.50 – 14.00	Lunch	Chancellors Conservatory
CONFERENCE END - DEPARTURE		

Information for delegates

Getting there:

By Train

Most Intercity trains call or terminate at Manchester Piccadilly Station. Either take a taxi (approx. 15 minutes) or take a five minute walk to Piccadilly Gardens Bus Station. More local rail services also stop at Manchester Oxford Road Station and Manchester Victoria Station.

From Manchester International Airport

Manchester International Airport is approximately 5 miles from Chancellors (about 20 minutes by taxi, which costs about £15-20 and is the most convenient route). If you wish to take the train from the airport there is a 24-hour service which runs 7 days a week, every 15 minutes during peak times and goes direct to Piccadilly Train Station. From the station either take a taxi or take the short walk to Piccadilly Gardens Bus Station and catch one of the many buses that follow the route to Wilmslow Road, Fallowfield.

By Bus from the City Centre

Take a bus numbered 41, 42, 42A, 43, 44, 48, 142, 143, 157, X57 from Piccadilly Gardens Bus Station to Wilmslow Road, Fallowfield. Walk to the junction with Moseley Road and turn left. At the next set of traffic lights turn left into Chancellors Way and the hotel is on your left, opposite the Armitage Sports Centre.

By Car Using GPS
Chancellors Hotel and Conference Centre has free on site car parking for hotel and conference guests. SatNav users should use the following postcode: M14 6ZT. This will lead you to Moseley Road, from Moseley Road turn onto Chancellors Way and Chancellors Hotel and Conference Centre is signposted on the left hand side across from the Armitage Sports Centre.

By Car from the North
Leave the M6 at Junction 20a (Lymm Interchange), onto the M56, following signs for Manchester Airport/City Centre. Take the right hand lanes at the end of the motorway where it becomes the A5103 - signposted Manchester City Centre. At the 5th set of traffic lights turn right onto Wilbraham Road (A6010 signposted Sheffield). At the 4th set of traffic lights turn left onto Chancellors Way. Chancellors Hotel and Conference Centre is situated on the left hand side opposite the Armitage Sports Centre.

By Car from the East
From the M62, leave at J18 (Simister Island) and follow the M60 S&E (Stockport). From the end of the M67 turn left/south onto the M60 S&E (Stockport). Leave the M60 at Junction 5 and join the A5103 - signposted Manchester City Centre. At the 5th set of lights turn right onto Wilbraham Road (A6010 signposted Sheffield). At the 4th set of traffic lights turn left onto Chancellors Way. Chancellors Hotel and Conference Centre is situated on the left hand side opposite the Armitage Sports Centre.

By Car from the South
From the M6, leave at J19 (Knutsford) and follow the A556 to Manchester. From the end of the A556 turn right onto the M56 following signs for Manchester Airport/City Centre. Take the right hand lanes at the end of the motorway where it becomes the A5103 - signposted Manchester City Centre. At the 5th set of traffic lights turn right onto Wilbraham Road (A6010 signposted Sheffield). At the 4th set of traffic lights turn left onto Chancellors Way. Chancellors Hotel and Conference Centre is situated on the left hand side opposite the Armitage Sports Centre.

Going to the Willowbank Hotel
The hotel is at 340 Wilmslow Road, which is to the south of Chancellors and on the opposite side of the road. From Wilbraham Rd turn right at the 3rd set of traffic lights onto Wilmslow Rd. The Willowbank Hotel is approx ¼ mile on the right. Postcode is: M14 6AF.

Going to Luther King House
Luther King House is on Brighton Grove, which is off Wilmslow Road to the north of Chancellors and on the same side of the road. From Wilbraham Rd turn left at the 3rd set of traffic lights onto Wilmslow Rd. Brighton Grove is approx ⅓ mile on the right. Postcode is: M14 5JP.

How to find:

Registration

Registration will be in the Reception area at Chancellors from 16.00 to 18.30 on Sunday 25th March (see map below). When you arrive, either go to registration, or if your accommodation is in the Willowbank Hotel or Luther King House you should check in there first (accommodation check-in available from 14:00 at all 3 locations). Please wear your conference badge at all times (including lunches/dinners).

Accommodation

Delegates staying at Luther King House (see map – blue footpath) or the Willowbank Hotel (see map – purple footpath) are within 10-15 minutes walking distance of Chancellors.

Chancellors Hotel and Conference Centre Chancellors Way Off Moseley Road Fallowfield Manchester M14 6ZT Tel: +44 161 907 7414 Email: chancellors@manchester.ac.uk	Luther King House Brighton Grove off Wilmslow Road Manchester M14 5JP Tel: +44 161 224 6404 Email: reception@lkh.co.uk	BEST WESTERN Willow Bank Hotel 340 Wilmslow Road Manchester M14 6AF Tel: +44 161 224 0461 Email: willowbank@bestwestern.co.uk

Lectures and posters

All lectures will be in the Flowers Lecture Theatre at Chancellors. Posters and exhibitors will be located in the meeting rooms around the lecture theatre.

Coffee breaks and receptions

All coffee breaks will be in Chancellors Conservatory and receptions will be in the Conservatory and the adjacent bar.

Meals

Dinner on Sunday, Monday and Tuesday will be in Chancellors' Carriage Restaurant. Lunches and Tea/Coffee breaks will be in Chancellors Conservatory. Delegates staying at Luther King House or the Willowbank Hotel will have breakfast at those locations, and delegates staying at Chancellors will have breakfasts in the Carriage Restaurant.

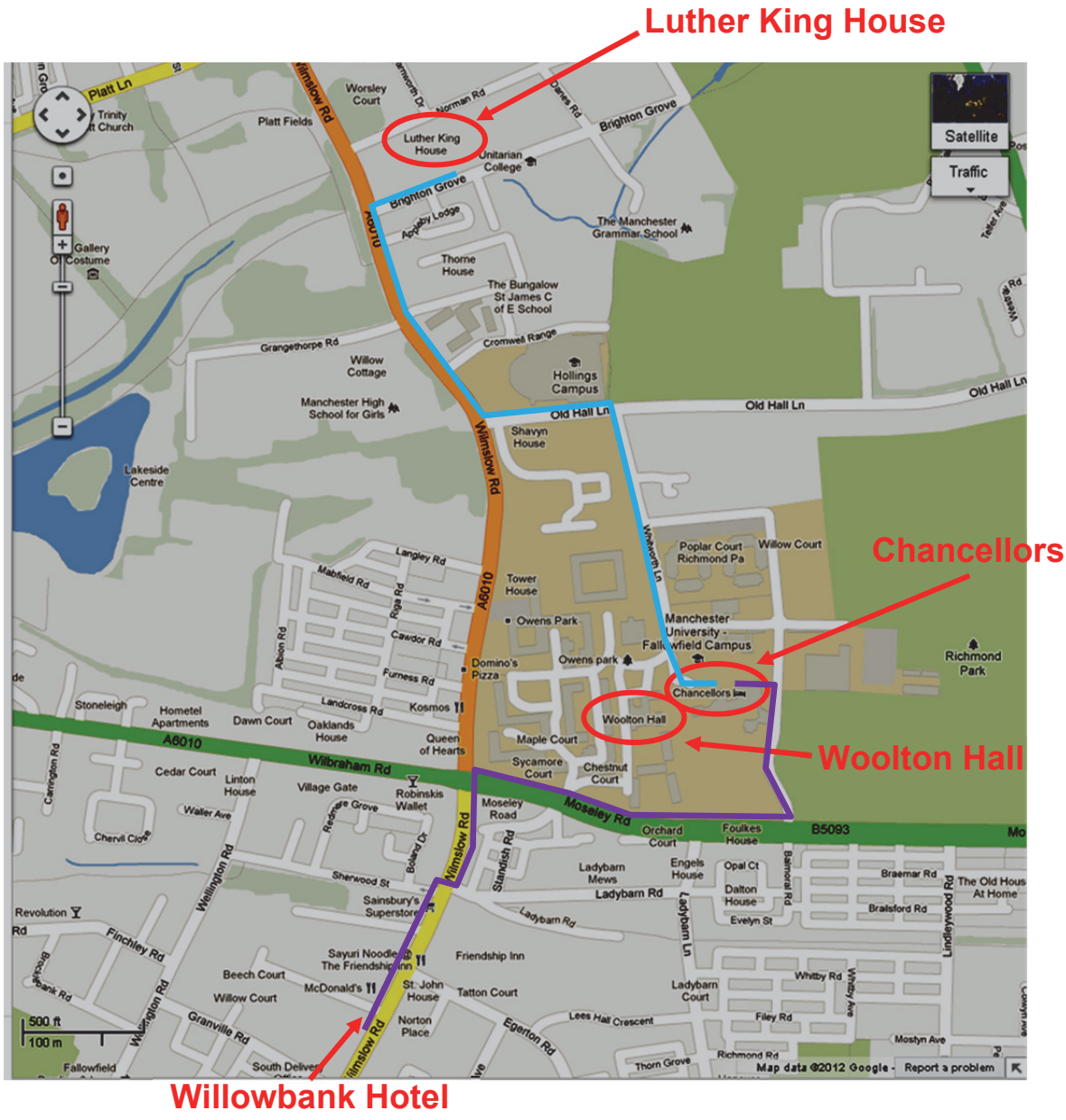
Banquet

The Conference banquet will be held on the Wednesday evening in Woolton Hall, a traditional University hall close to Chancellors Conference Centre on the Fallowfield part of campus (see map for footpath).

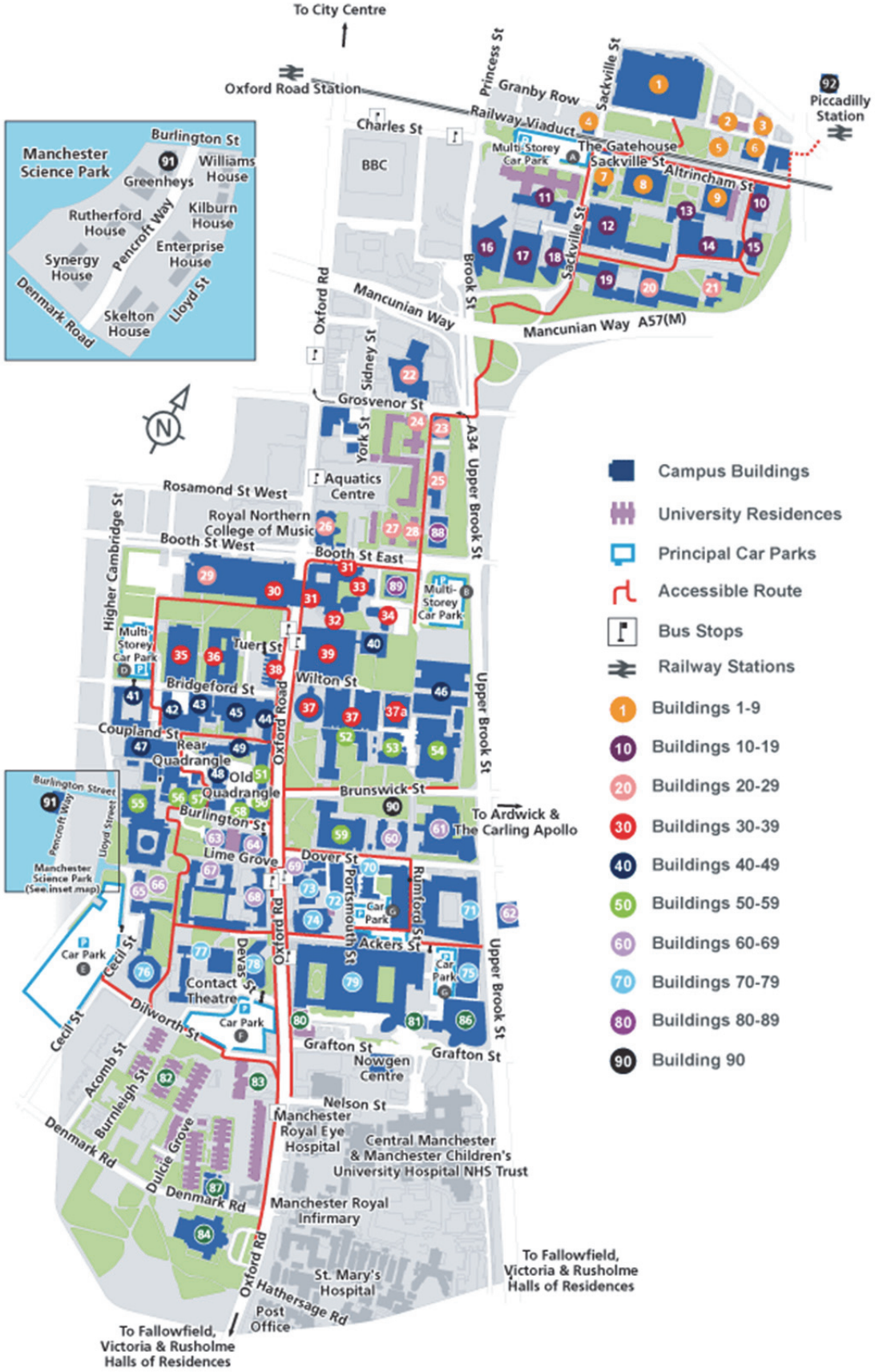
Shops

There are a number of small shops located on Wilmslow Rd close to Chancellors Hotel and Conference Centre, including a Pharmacy – because this is a student area, they have extended opening hours. There is also a large branch of Sainsburys located on Wilmslow Rd, just past the junction with Moseley Rd on the left. Opening hours are 8am to 11pm (11am to 5pm Sundays).

Map of Conference venue



University of Manchester Campus Map



Speaker information

All lectures will be held in the Flowers Lecture Theatre. A PC with PowerPoint and a projector will be provided. It will also be possible to attach a speaker's laptop to the projector. A laser pointer will be provided. If you need any other equipment, please inform the conference organiser. **Please upload your presentation and/or test your laptop the day before your talk if at all possible.**

The length of lectures is 60, 30, 20 and 15 min for Bruker, Keynote, Invited, and all other lectures, respectively. Additional 5 min are allocated at the end of each lecture (except Bruker lecture) for questions.

Poster presenter information

Posters will be displayed in the Marquis and the Morley rooms adjacent to the Flowers Lecture Theatre. Poster boards are **A0 portrait format**. They can be set up on Monday morning from 08.00, and will have to be taken down on Thursday before or shortly after lunch. Drawing pins will be provided to attach the posters to the boards.

Poster numbers will be displayed on the boards. There will be two poster sessions at the conference, for even and odd posters. However, the posters will be on display throughout the conference, and coffee breaks/receptions will be held near the posters.

Poster prizes are sponsored by Wiley, Springer and the RSC

Internet access

There is free WiFi internet access at Chancellors Hotel and Conference Centre, Luther King House and the Willowbank Hotel. Delegates wishing to connect to the internet must bring their own laptops – connection information will be available at each location from reception.

Car parking

Chancellors Hotel and Conference Centre has ample free on site car parking for hotel and conference guests. There is also free parking at the Willowbank Hotel (there is normally a charge for this, but it will be waived for conference delegates) and at Luther King House.

Taxis

Contact reception at Chancellors or your accommodation to ask for a Taxi to be booked for you. Alternatively, Mantax Black Cabs pass along Wilmslow Rd very frequently and will stop on request. Mantax can be contacted directly on 0161 230 3333. Please do not use private hire cars unless they have been booked in advance.

Checking out and left luggage

The delegates will need to check out of their rooms **by 10.00 on the day of departure** (Thursday). It will be possible to store the luggage in a room at

Chancellors, the Willowbank or Luther King House on Thursday until the end of the conference.

Accompanying persons

The registration fee for accompanying persons includes all lunches / dinners / banquet / receptions. Whilst there is no specific programme for accompanying persons, Manchester has much more to offer and a number of leaflets with details of local attractions have been included in the delegate packs. Admission is free to most of these attractions, other than for special exhibitions.

Information centre: Visit Manchester (http://www.visitmanchester.com/) can provide further information about other local attractions and is located on Portland St, close to Piccadilly Gardens Bus Station. See also links below.

Manchester Cathedral is located on the northern side of the City Centre and whilst it does not have the medieval heritage of the great gothic cathedrals, it is well worth a visit.

Museums: Manchester Museum, Whitworth Art Gallery, John Rylands Library, Museum of Science and Industry, Manchester City Art Gallery, Imperial War Museum North, The Lowry, Gallery of Costume (Platt Hall), Jodrell Bank Discovery Centre (requires a car to get there).

Theatres: Royal Exchange, Library Theatre, The Lowry, Palace Theatre, and Opera House.

Free afternoon in Manchester – Tuesday 27th March

Following the tradition of our conferences, Tuesday afternoon will be free from lectures (the Bruker lecture will be scheduled in the evening). The delegates are invited to explore Manchester's many attractions, and we recommend in particular the Museum of Science and Industry. As in most British museums these days, the entry is free of charge.

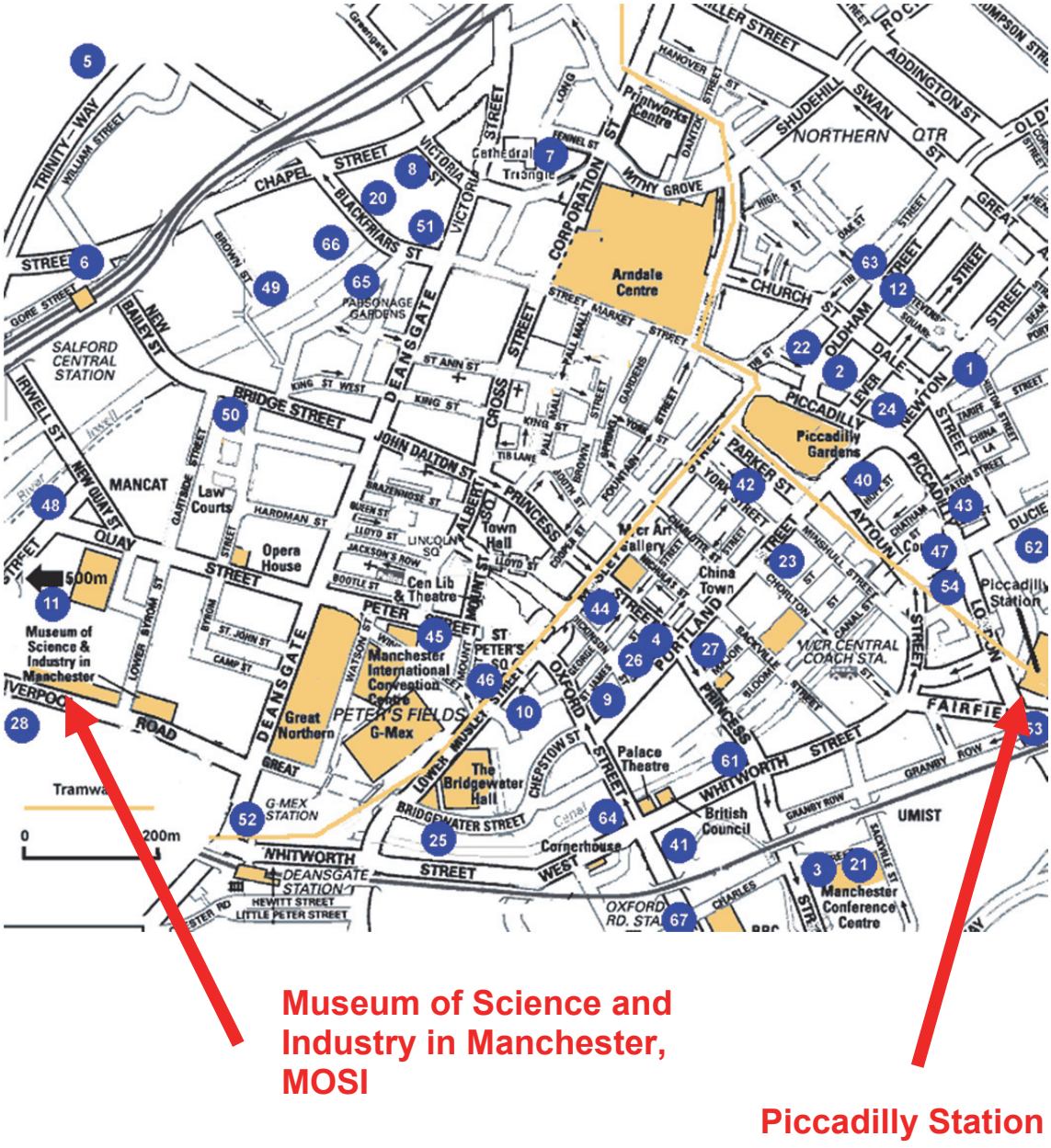
Local places of interest: http://www.museum.manchester.ac.uk/ (Manchester Museum) http://www.whitworth.manchester.ac.uk/ (Whitworth Art Gallery) http://www.jodrellbank.net/ (Jodrell Bank Discovery Centre) http://www.mosi.org.uk/ (http://north.iwm.org.uk/ (Imperial War Museum North)Museum of Science and Industry)	http://www.thelowry.com/ (The Lowry – Art Gallery and Theatre complex) http://www.manchestergalleries.org/ (Manchester City Art Gallery) http://www.manutd.com/en/Visit-Old-Trafford/ (Manchester United) http://www.mcfc.co.uk/The-Club/Stadium-tours/ (Manchester City)

Manchester started life as a Roman settlement, but turned into the world's first great industrial city during the industrial revolution of the 18th and 19th centuries, even being the site of the world's first railway station. It has a proud history in science and technology, the famous firsts including splitting of the atom and creation of the first programmable computer. Manchester has

undergone a great deal of redevelopment over the last couple of decades and is now the 3rd most popular tourist city in the UK.

Buses numbered 41, 42, 42A, 43, 44, 48, 142, 143, 157, X57 from Wilmslow Road Fallowfield (on the far side of road from Chancellors Hotel Conference Centre) will take delegates into the City Centre and a map showing the bus routes and tourist attractions is included in the delegate pack. The Whitworth Art Gallery and Manchester Museum are located on the way into the City Centre. See the above section for accompanying persons for information about further Manchester attractions.

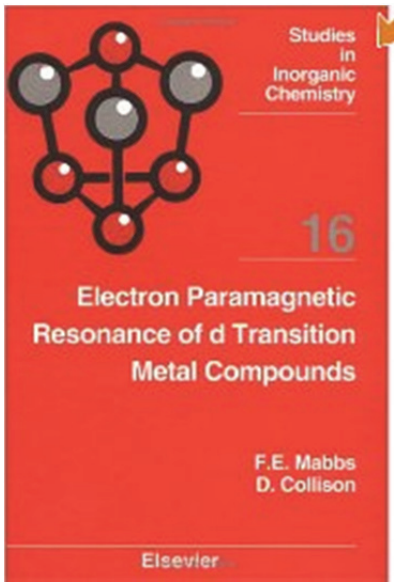
Manchester City Centre Map



We thank the Sponsors of the Conference:

EPR @ Manchester

The University of Manchester currently hosts the EPSRC funded UK National EPR Service. The current contract was awarded in October 2010, with an equipment base that includes two pulse platforms (S-, X-, Q-bands), and four c.w. platforms (L-, S-, X-, K-, Q-, W-). The EPR Service moved from three separate basement labs in the Chemistry Building to a single suite in a new laboratory within the Photon Science Institute. This has the additional benefit of allowing helium recycling and a stronger interaction with physicists and electrical engineers. The interdisciplinary interaction has led to ODMR at 34 GHz being added to the Service in collaboration with Bruce Hamilton, Nigel Poolton and Brian Towlson. A 300 mK cryostat is currently being developed with Lucio Piccirillo, funded by an EPSRC grant. Bruker has also funded an Application Scientist post for five years, which will begin in May 2012 with the arrival of Alistair Fielding from Göttingen. The EPR Service is delivered by an excellent team of post-doctoral fellows – Dr Floriana Tuna and Dr Stephen Sproules - and technical support from Dan Sells. Other research projects in EPR spectroscopy involve PhD students Chloe Stott, Morten Albring and James Walsh, and a new post-doctoral worker, Fabrizio Moro, is about to arrive from Nottingham.



Manchester has a long tradition in EPR spectroscopy. In 1964 Frank Mabbs installed X- and Q-band Varian spectrometers in the basement of the then "new" Chemistry building. David Collison joined the EPR group in 1979, along with the arrival of a Varian E-112 X- and Q-band spectrometer. Some of the earliest general spectrum simulation software was developed here, initially on punch cards. Frank's and David's textbook on the EPR of d-transition metal complexes appeared in 1992, and is used world-wide as an authoritative tome and door-stop.

In 1995 Manchester was awarded the EPSRC National Service for EPR spectroscopy, jointly with Cardiff specialising in ENDOR spectroscopy. The first post-doc appointed to the Service in Manchester was Eric McInnes, and the new Bruker systems installed at that point allowed L-, S-, X-, K- and Q-band continuous wave spectroscopy. Over the following fifteen years the Service was renewed several times, including high field spectroscopy in St Andrews with Peter Riedi and his then post-doc Graham Smith, followed by arrival of a Bruker W-band spectrometer in Manchester in 2005.

Manchester hosted the RSC ESR conferences in 1998 and 2003. David has been the Chair of the RSC ESR group and Eric is currently its Secretary. Eric won the International EPR Society's Young Investigator Award for 2005.

Bruker prize lecture and reception

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

The Bruker Lectureship for 2012 has been awarded to:

Kev Salikhov

Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan, Tatarstan.

The lecture will take place on Tuesday 27th March in the Flowers Lecture Theatre at 19.30, followed by the Bruker-sponsored Wine Reception in the Chancellors Conservatory and a Free Bar also kindly sponsored by Bruker. The title of Bruker lecture 2012 will be:

Quantum computing on electron spins using the pulse EPR spectroscopy methodology

Previous winners of the Bruker Lectureship:

1986	M. C. R. Symons	**1995**	H. M. McConnell	**2004**	W. L. Hubbell
1987	K. Möbius	**1996**	B. M. Hoffman	**2005**	K.-P. Dinse
1988	H. Fischer	**1997**	K. A. McLauchlan	**2006**	Yu. D. Tsvetkov
1989	J. S. Hyde	**1998**	J. R. Pilbrow	**2007**	D. Goldfarb
1990	J. H. Freed	**1999**	J. Schmidt	**2008**	E. J. J. Groenen
1991	E. de Boer	**2000**	D. Gatteschi	**2009**	G. Jeschke
1992	G. Feher	**2001**	J. Hütterman	**2010**	R. P. Mason
1993	N. M. Atherton	**2002**	G. R. & S. S. Eaton	**2011**	T.F. Prisner
1994	A. Schweiger	**2003**	W. Lubitz		

JEOL student prize lectures

The JEOL competition is open to postgraduates in their 2nd or 3rd year and postdoctoral fellows in their 1st year. The 15 minutes lectures are judged by the ESR Spectroscopy Group Committee on the basis of their scientific content and delivery. An engraved medal and monetary prize are generously provided by JEOL for the winner of the presentation, to be presented at the conference banquet.

This year, the competition will take place during the Monday afternoon session.
The 2012 lectures, selected on the basis of the abstracts submitted, will be:

Utilizing the TWT linear region: Double Electron-Electron Resonance (DEER) with multiple excitation pulses and dead-time free three-pulse DEER

Alice Bowen

Centre for Advanced Electron Spin Resonance, Oxford University., UK

A Novel Triple Resonance Correlation Sequence for Resolving and Assigning Signals in ELDOR-Detected NMR Spectra

Ilia Kaminker

Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

EPR/HYSCORE and DFT study of nickel adducts with O2, CO and NO molecules encaged in zeolites

Tomasz Mazur

Faculty of Chemistry, Jagiellonian University, Krakow, Poland

Microcrystalline Silicon: Orientation dependence of light induced EDMR signals

Christoph Meier

Fachbereich Physik, Freie Universität Berlin, Berlin, Germany

Trityl: A new spin label for nanometer distance Measurements

Gunnar W. Reginsson

University of St Andrews, BSRC, UK

The wine reception in Chancellors Conservatory and bar on Monday evening is kindly sponsored by JEOL, followed by a Free Bar, also kindly sponsored by JEOL.

Committee of the ESR Spectroscopy Group of the Royal Society of Chemistry

Dr Mark Newton (Chair)	University of Warwick	2010-2013
Prof Eric McInnes (Secretary)	University of Manchester	2011-2015
Dr Fraser MacMillan (Treasurer)	University of East Anglia	2010-2014
Dr Ilya Kuprov (Web Master)	University of Southampton	2009-2012
Dr Tim Smith (Industry Representative)	Jeol Corporation	2011-2013
Dr Chris Kay (Retiring Secretary)	University College, London	2011-2012
Dr David Norman	University of Dundee	2009-2012
Dr Christiane Timmel	University of Oxford	2009-2012
Dr Graham Smith	University of St Andrews	2010-2013
Dr Dima Svistunenko	University of Essex	2010-2013
Dr Helen Williams	AstraZeneca	2010-2013

David Collison and Eric McInnes acknowledge the help of people at Manchester who assisted with the organisation of the conference:

Prof Richard Winpenny
Dr Kathy England
Cassandra Kenny
Sarah Evans
Gill Smith

THE UNIVERSITY OF WARWICK

2013

46th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry

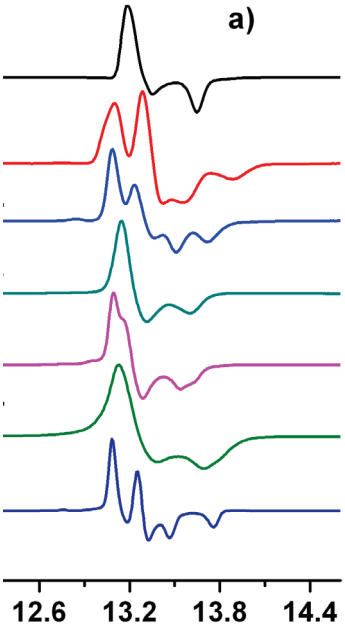
Sunday 7th to Thursday 11th April 2013

EPR Studies of Rings and Dimers of Rings

*Richard E. P. Winpenny**
School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester UK.
e-mail: richard.winpenny@manchester.ac.uk

Heterometallic rings have proven to be outstanding objects for physical studies, including EPR spectroscopy.[1] They can be used to study phenomena such as quantum oscillations of the total spin at avoided crossings,[2] and used to examine the validity of modeling EPR spectra in the strong exchange limit.[3] We have also used them to look at phase memory times in molecular magnets.[4]

In this talk results on single rings will be discussed – probably including studies of nine-metal rings looking for new frustration effects. Results on dimers of rings will also be described.[5]



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Intercluster exchange interactions and spin state switching in copper-nitroxide based molecular magnets $Cu(hfac)_2L^R$ studied by EPR

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Design of thermo- and photo-switchable molecular magnetic compounds attracts significant attention due to potential applications in nanotechnology. Polymer-chain complexes $Cu(hfac)_2L^R$ (often called "breathing crystals") are formed by copper(II) hexafluoroacetyl acetonates ($Cu(hfac)_2$) and stable nitronyl nitroxides (L^R) or tert-butylpyrozolylnitroxides (L^R_{tert}). These compounds undergo reversible structural rearrangements accompanied by magnetic susceptibility changes similar to a classical spin crossover, where the exchange-coupled three-spin cluster nitroxide-copper(II)-nitroxide changes its spin configuration between weakly-coupled and strongly-coupled spin states. This spin state switching, as well as intra- and intercluster exchange interactions, can be efficiently studied using EPR [1].

In this work we have studied intercluster exchange interactions and spin state conversion in series of "breathing crystals" using Q-band EPR. In our previous work [1] we demonstrated that the intercluster exchange interactions occur between adjacent polymer chains due to the delocalization of electron spin density in nitronyl nitroxide, and that the direction of magnetic "chains" does not coincide with the direction of structural polymer chains. Here we investigated angular dependence of the line width of spin triad in detail and observed the behaviour characteristic for 1D magnets. We studied the topology of magnetic chains and compared it for several compounds. The direction of magnetic chains and functional properties of "breathing crystals" can be tuned chemically. We have demonstrated that the modification of radical ligand from L^R to L^R_{tert} in three compounds $Cu(hfac)_2L^R_{tert}$ (R=Me, Et, Pr) leads to a change of the direction of magnetic chains [2]. EPR signals of one-spin copper ions and triads become exchange-narrowed, meaning that the intercluster exchange coupling within the same polymer chain has dramatically increased compared to the previously studied compounds. Using an approach of the modified Bloch equations, we obtained satisfactory agreement of computational modelling with experimental spectra. We have also estimated intercluster exchange interaction based on the observed line shape of spectra and theoretical modelling. Finally, we have observed the Light-Induced Excited Spin State Trapping (LIESST) phenomenon in these new compounds $Cu(hfac)_2L^{Me}_{tert}$. The lifetime of the excited state depends on the sample preparation procedure and can reach hours at temperature around 60 K that is significantly higher compared to our previous LIESST studies.

This work was supported by RFBR (No. 11-03-00158), the RF President's Grant (MK-1662.2012.3, MK-868.2011.3).

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Quantum operations by pulsed ESR spectroscopy: Molecular design for biradical and triradical qubits

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The last decade has witnessed that the emerging field of quantum computing and quantum information processing (QC/QIP) is linked to chemistry in spite of the fact that molecular electron spin qubits are the latest arrival amongst many physical qubits. Physical realization of scalable quantum computers (QCs) and quantum simulators has been the focus of current subjects in order to experimentally verify various theoretical ideas [1,2].

In this work, we have treated two and three electron-spin qubit systems, in which electron-spin qubits weakly interact via electronic exchange interactions. We have designed and prepared such weakly exchange-coupled stable biradical (**1**,**2**) and triradical (**3**) systems as synthetic electron spin-qubits, for the first time magnetically diluted in the corresponding ketone-based crystals. The molecular design is based on *g*-tensor engineering for **1** and **3** and hyperfine engineering for **2** in the oriented systems. We exploit the electron spin dipolar interactions of the qubits to execute quantum gate operations by the use of pulsed ESR technology. All the spin dipolar interactions have experimentally been determined. As expected, the *D* value for **2** is larger than that for **1**, corresponding to a shorter distance between the electron spins in **2**. As a result, we can accelerate CNOT gate operations in **2** in a shorter time than in **1.**

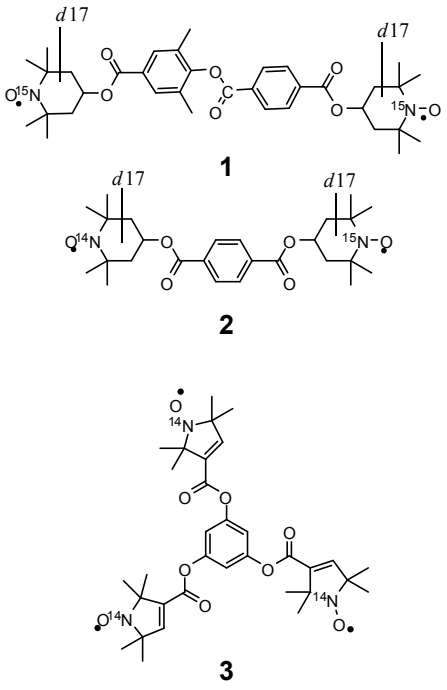

Figure 1. Synthesized molecular electron spin two-qubit and three-qubit systems

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Relaxation Enhancement in Orthogonal Spin Pairs – Precision and Short Distance Limitation –

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Distance information obtained by magnetic resonance is mainly extracted from dipole-dipole interaction of two spatially separated spins. The distance can either be measured directly from the dipolar interaction frequency [1,2] or indirectly via the change of the relaxation times of the interacting spins. [3] In the present work we determine distances in an orthogonal spin pair, consisting of a nitroxide radical and a Dy^{3+} ion, via relaxation enhancement (RE). We discuss the performance and the reliability of RE based distance measurements.

Comparison with Gd^{3+} - nitroxide DEER [4] data obtained on the same α-helical polypeptide reveals an underestimation of distances determined by RE. We investigate the impact of the r^{-6} averaging arising for the applied single distance approach. This r^{-6} averaging induces a shift of the apparent mean distance towards smaller values. Furthermore, we illustrate the influence of the experimental inversion recovery pulse sequence on the observed suppression of short distances and propose an empirical suppression function, which represents this behaviour, and give an estimate for the minimal detectable distances.

The magnitude of the RE effect is affected by the external magnetic field. This allows for decreasing the suppression limit by working at Q-band frequencies instead of the routinely used X-band frequencies. Additionally, simulations of Dy^{3+} induced RE show that the assumption of isotropic orientation averaging can be applied even at the short distance limit, where suppression effects are dominating.

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Quantum control of hybrid nuclear-electronic qubits

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Pulsed magnetic resonance allows the quantum state of electronic and nuclear spins to be controlled on the timescale of nanoseconds and microseconds respectively. The time required to flip either dilute electronic or nuclear spins in silicon is orders of magnitude shorter than their decoherence times [1-3], leading to several schemes for quantum information processing [4, 5].

We have proposed that qubit control could be speeded up and decoherence slowed down when the eigenstates approximate 50:50 superpositions of the electronic and nuclear spin states [6]. This hybrid regime can be accessed with bismuth dopants in silicon (Si:Bi) using a 4 GHz spectrometer because of the large hyperfine coupling of 1.475 GHz and the large nuclear spin of $^{9}/_{2}$. Here we use Si:Bi to demonstrate quantum control of hybrid nuclear-electronic states for the first time, in just 32 ns [7]. This is orders of magnitude shorter than previous experiments where nuclear states were used [1, 2]. The coherence times of our states are five orders of magnitude longer, reaching 4 ms, and are limited by the naturally-occurring ^{29}Si nuclear spin impurities [7].

We used a pulsed 4 GHz EPR spectrometer at ETH Zurich [8] and benefited from preliminary CW measurements at the National EPR Facility & Service at the University of Manchester.

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EPR of Fe^{3+} centres in $SrTiO_3$: Monodomain crystals to thin films

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The substitutional incorporation of Fe^{3+} ions in $SrTiO_3$ has provided the clearest example of charge compensation of an acceptor ion in a perovskite oxide, ABO_3, material, hence is an established model system for B-site acceptor doping in defect chemistry. Fe^{3+} substitutes for Ti^{4+} in cubic phase $SrTiO_3$, either within a complete oxygen octahedron, giving cubic centre [1], or at an octahedron with a single oxygen vacancy which results in centre with marked axial symmetry[2]. There has been a recent resurgence of interest in these centres as they may provide insight on the mechanisms of resistive switching devices[3], and more generally provide a mechanism for monitoring oxygen vacancy behaviour[4, 5].

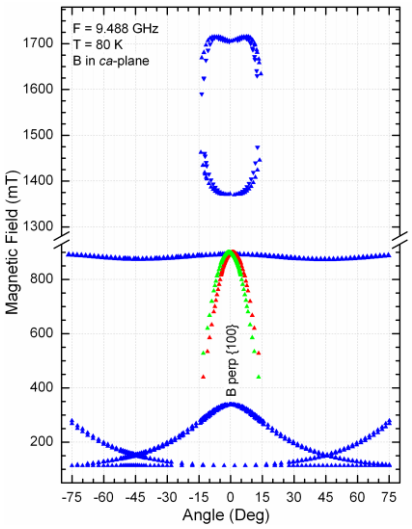

Figure 1. Fe^{3+}-V_O centre monodomain crystal roadmap.

Here we establish the complete spin-Hamiltonian parameters for both centres to fourth order, both in the cubic and the low temperature antiferrodistortive tetragonal phases. A crystal shaped so as to transform to a monodomain sample in the tetragonal phase was used, and simplify the SH determination. It is also found that above the transition temperature, in the cubic phase, the residual strain is sufficient to orient the isolated Fe^{3+} centres, which exhibit a small axial component.

The measurements are extended to a series of pulsed laser grown Fe-doped $SrTiO_3$ thin films grown on Nb-doped $SrTiO_3$ substrates. Fe^{3+} resonances are identified and characterised.

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Spying with Mn^{2+} ions the structure changes during the thermal decomposition of $Zn_5(CO_3)_2(OH)_6$ and $Zn(OH)_2$ into nanostructured ZnO

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National Institute of Materials Physics, Magurele, Romania.

Nanostructured ZnO doped with transition metal ions (TMIs), which is expected to present high temperature ferromagnetism, is a promising candidate for applications in spintronics [1]. The difficulties in homogeneously doping with TMIs can be overcome by the thermal decomposition of inorganic precursors, such as hydrozincite ($Zn_5(CO_3)(OH)_6$), which can be much easier doped [2]. EPR spectroscopy of trace amounts of Mn^{2+} ions can offer detailed information on changes in the structure and chemical composition during the thermal decomposition of the precursors in pulse annealing experiments, by employing advanced procedures and software for the accurate analysis of the resulting spectra [3].

We show for the first time that the decomposition of hydrozincite in air/vacuum, which takes place in a narrow temperature range below 225^0C/175^0C, is a two steps process involving an amorphous-crystalline structural transformation. Thus, the disordered, practically amorphous ZnO, which is initially formed by the decomposition of hydrozincite, further transforms into nanocrystalline ZnO of increasing particles size and crystallinity with temperature increase. The presence of a sizable fraction of amorphous ZnO, even by annealing at T = 650^0C, should be considered in the analysis of the physical-chemical properties of the resulting nanostructured ZnO [4].

Unlike hydrozincite, EPR studies have shown that the thermal decomposition of crystalline $Zn(OH)_2$, a material involved in the high temperature synthesis of ZnO, is a one step process which takes place in air in the 110-130^0C range [5]. It results in nanocrystalline ZnO containing a rather large amount of point defects.

Complementary XRD, TEM and thermal analysis measurements on the EPR investigated samples have confirmed our conclusions in both cases. The observed differences in the structure and defect properties of the nanostructured ZnO resulting from the two precursors can be explained by differences in the bonds breaking process.

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Elucidating the Nature and Reactivity of Metal Ions Incorporated in the Framework of Aluminophosphate Molecular Sieves. New Evidences from HYSCORE and Pulse-ENDOR Spectroscopy.

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The incorporation of transition metal ions (TMIs) into framework sites of porous and mesoporous materials is a key strategy in the quest for new materials with novel and controlled chemical and catalytic properties. A relevant example is that of aluminophosphate molecular sieves, AlPOs, which are microporous zeotype materials with neutral lattices and a wide range of structural diversity. Among the large variety of different TMIs, Ti-doped and V-doped AlPOs are particularly interesting due to the specific activity of isolated tetrahedral Ti and V sites towards different chemical and photochemical processes. Despite the importance of these metal centers and the crucial role played by their local coordination, evidence for isomorphous substitution is often indirect and much speculation is present about this topic.

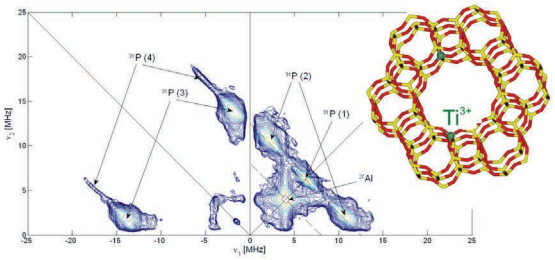

Figure 1. Experimental HYSCORE spectra recorded at 5K of reduced TiAlPO-5. In the inset the structure of AlPO-5 is shown.

In this communication, we show that advanced EPR methods (HYSCORE and Pulse ENDOR spectroscopies) can provide unique and unambiguous evidence on the specific framework sites at which paramagnetic TMIs are incorporated, allowing to monitor in detail their local environment and their subsequent chemical reactivity. In particular for both Ti and V doped AlPO-5 systems we report the first observation of large ^{31}P hyperfine couplings, which, combined with the absence of specific ^{27}Al couplings, provide direct evidence for framework substitution of Ti and V at Al sites. Moreover in the case of Ti-AlPOs, we demonstrate that these very sites are coordinatively unsaturated and chemically accessible, following in detail the chemical reactivity towards H_2O, NH_3 and O_2.

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Utilizing the TWT linear region: Double Electron-Electron Resonance (DEER) with multiple excitation pulses and dead-time free three-pulse DEER.

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DEER is a well-established technique for the measurement of distances between Nitroxide spin labels in biological systems. Most commonly used is the four-pulse sequence with a single pump frequency and detection frequency. This experiment, however, is not optimal for all systems. Here we present two variants on the DEER experiment that both lead to an improvement in the quality and sensitivity of the spectra recorded.

Repeated Excitations IN DEER (REINDEER) [1]: Conventional DEER uses two frequencies, one to pump the spins and the other to detect. At X-band and higher frequencies pulses (typically tens of nanoseconds in length) do not excite the entire EPR spectrum for both Nitroxides and metal centres; as a result the experimental sensitivity is lower than the theoretical maximum. We have addressed this shortcoming through the use of additional microwave sources to increase the frequency spectrum of the pump pulse. Data collected using multiple pump frequencies is shown to have a large increase in modulation depth and corresponding signal-to-noise ratio.

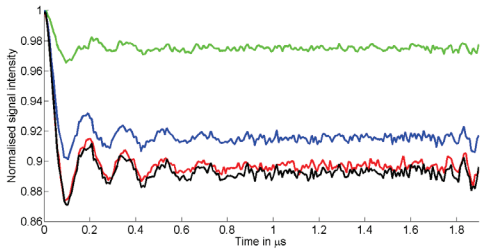

Figure 1. Increase in DEER modulation depth achievable with the use of multiple pump pulse frequencies for a dinitroxide system. Green and blue traces, single pump frequencies: detection on $m_I = 1$ and pump on $m_I = -1$ and $m_I = 0$ respectively. Red trace, two pump frequencies: detection on $m_I = 1$, pump on $m_I = -1$ and $m_I = 0$. Black trace: the multiple of green and blue traces.

Dead-time free three-pulse DEER [2]: Three-pulse DEER has a great potential advantage over the four-pulse sequence by allowing much longer time traces to be recorded with comparable signal to noise. However, the four-pulse DEER technique has the benefit of being inherently dead-time free unlike the three-pulse variant. Here we examine the source of the three-pulse DEER dead-time, which is primarily due to non-linearity in the TWT amplifier's input and output power. We suggest how these problems can be overcome using the standard 1 kW TWT and a 2 mm split ring resonator (MS2). The experimental work is supplemented by density matrix simulations.

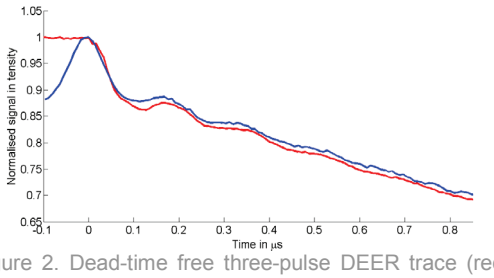

Figure 2. Dead-time free three-pulse DEER trace (red) and a corresponding four-pulse DEER trace (blue).

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A Novel Triple Resonance Correlation Sequence for Resolving and Assigning Signals in ELDOR-Detected NMR Spectra

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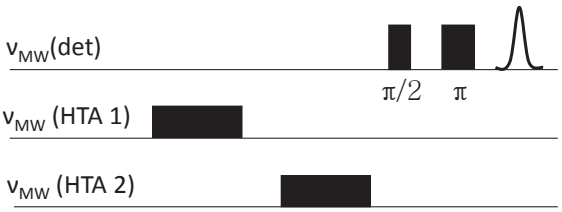

Hyperfine spectroscopy consists of pulsed EPR methods for determining small hyperfine couplings that are not resolved in conventional continuous wave or echo detected EPR spectra. Two such popular techniques are Electron – Nuclear Double Resonance (ENDOR) and Electron Spin Echo Envelope Modulation (ESEEM) experiments. When ENDOR or ESEEM spectra are too congested, or when correlation between different lines is of interest, extra information is gained from spreading the information into a second spectral dimension. An extensively used and very popular such two dimensional (2D) experiment is HYSCORE (hyperfine sublevel correlation spectroscopy) that is a 2D analog of ESEEM. Another example is the TRIPLE experiment that correlates ENDOR lines. ELDOR (electron-electron double resonance)-detected NMR is another Hyperfine spectroscopy method. It relies on direct excitation of forbidden EPR transitions by intense microwave irradiation and is particularly useful at high magnetic fields where the nuclear frequencies are better resolved. The resolution of this experiment is limited by the electron spin phase memory time and it is therefore particularly useful for quadropolar nuclei such as ^{14}N and ^{17}O where there is significant state mixing, yielding high S/N, and lines are intrinsically broad.

In this work we present a novel 2D triple resonance pulsed EPR experiment, based on ELDOR-detected NMR, shown in the figure, where the echo intensity is measured as a function of the frequency of the two HTA pulses. It provides correlations between different lines in ELDOR-detected NMR spectra. This new triple resonance experiment was implemented on W-band (95GHz) spectrometer. First we demonstrate this experiment on a nitroxide spin labeled polyethylene oxide spin probe in block copolymer micellar solution where correlations between the nitroxide ^{14}N single quantum and double quantum transitions within the same and different electron manifolds are observed. These different types of correlation can be distinguished because the former give positive peaks and the latter negative ones. Next we present 2D – ELDOR detected NMR spectra acquired in the ^{63}Cu ^{33}S labeled and natural abundance Azurin proteins. This allows clear distinction between ^{33}S and ^{14}N signals that overlap in the 1D ELDOR detected NMR spectra.

EPR/HYSCORE and DFT study of nickel adducts with O_2, CO and NO molecules encaged in zeolites

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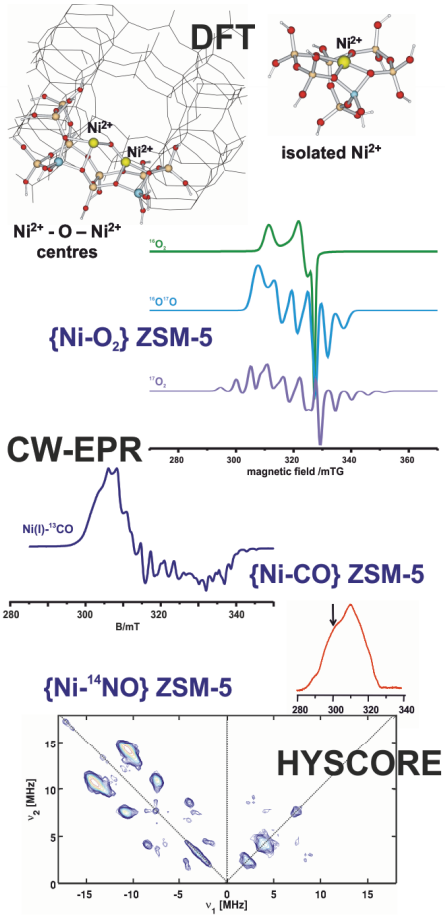

The paramagnetic mononuclear nickel adducts with small molecules $\{NiXY\}^n$ are the key species implicated in various important homo- and heterogeneous catalytic systems including enzymatic processes. For the in-depth understanding of the fundamental chemistry of the $\{NiXY\}^n$ units for accurate control of its reactivity, a detailed atomic level description of the electronic and magnetic structure of these species in discrete and embedded states is of great cognitive value. Due to the paramagnetic nature of the many of the $\{NiXY\}^n$ species EPR has widely been used in this purpose.

Herein, we report the results of continues wave CW-EPR and pulsed (HYSCORE) spectroscopies corroborated by quantum chemical investigations that have led to the observation of paramagnetic adducts: $\{Ni(^{12,13}CO)_m\}^9$, $\{Ni^{14,15}NO\}^{10}$, $\{Ni^{16,17}O_2\}^{11}$. Using relativistic density functional theory methods such as zeroth-order regular approximation (ZORA) or spin-orbit mean-field approximation (SOMF), we provided a detailed theoretical account for the electronic and magnetic structure of the investigated adducts, and their speciation. In view of the variety of local environments within which the $\{NiXY\}^n$ units may reside, we investigated more closely the molecular nature of the ***g***, hyperfine (^{17}O), superhyperfine ($^{14,15}N$, ^{13}C) and quadruple tensors (^{27}Al) in terms of the local symmetries and the coordination states. By means of the ETS-NOCV approach 3 orbital channels (σ, π, and δ) of congruent and incongruent charge and spin density flows within the $\{NiXY\}^n$ units, contributing jointly to the activation of the attached XY molecule, were identified.

Acknowledgment: T.M. thanks for the support from the International PhD studies program at the Faculty of Chemistry, Jagiellonian University, within the MPD Program of the Foundation for Polish Science co-financed by the EU Regional Development Fund. K.P. thanks for the financial support from the „Society – Environment –Technologies" project at the Jagiellonian University in the framework of the EU Social Fund.

Microcrystalline Silicon: Orientation dependence of light induced EDMR signals

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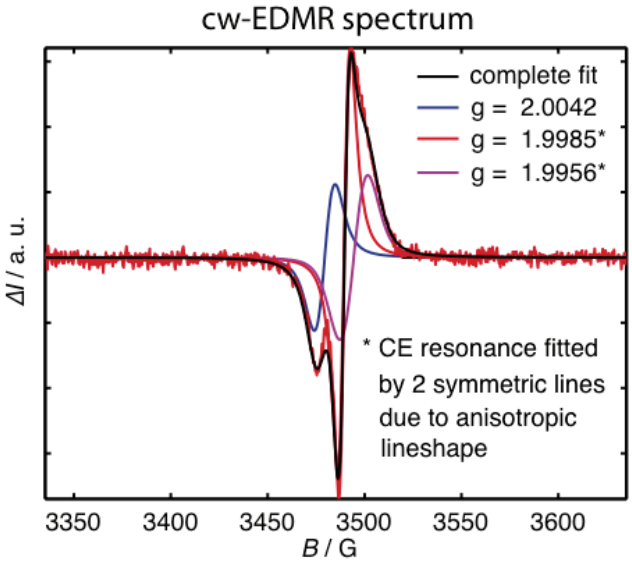
Microcrystalline silicon (µc-Si:H) is a promising material for thin-film solar cells due to cost and production advantages compared to crystalline silicon (c-Si). It is characterised by a partly disordered structure with embedded silicon crystallites. Defects in the bulk and at interfaces as well as localised states close to energy band edges give rise to charge carrier loss and hopping processes influencing the device efficiency.



Charge carrier transport channels and the EPR fingerprints of contributing defect centres were analysed by electrically detected magnetic resonance (EDMR) in order to elucidate the correlation between morphological structure and the electrical properties. This technique detects changes in sample conductivity induced by spin manipulation resulting in significantly enhanced sensitivity compared to conventional microwave absorption detection.

Continuous-wave EDMR was applied to fully processed µc-Si:H thin-film solar cells to analyse dependencies of EDMR signals on the magnetic field orientation. With preparatory studies including temperature and modulation phase dependent experiments it was possible to extract four different spectral contributions. Using this knowledge we concentrated on the two main resonances for angle dependent measurements (see figure). The signal at g ~ 2.004 can likely be attributed to localised states near the conduction band edge in the amorphous phase [1]. The signal at g ~ 1.998 coincides with the so-called CE resonance detected in EDMR and EPR spectra of highly n-doped or illuminated µc-Si:H [1,2]. The location and character of this CE-type resonance are not identified yet. Further orientation-dependent measurements will aid to assign this signal to the crystalline or amorphous phase of this heterogeneous material.

[1] J. Behrends et al., *Philosophical Magazine,* 2009, 89, 2655-2676.
[2] F. Finger et al., *Philosophical Magazine Letters,* 1994, 70, 247-254

Acknowledgments: This work was supported by the German Federal Ministry of Education and Research (BMBF network project EPR-Solar 03SF0328C).

Trityl: A new spin label for nanometer distance measurements

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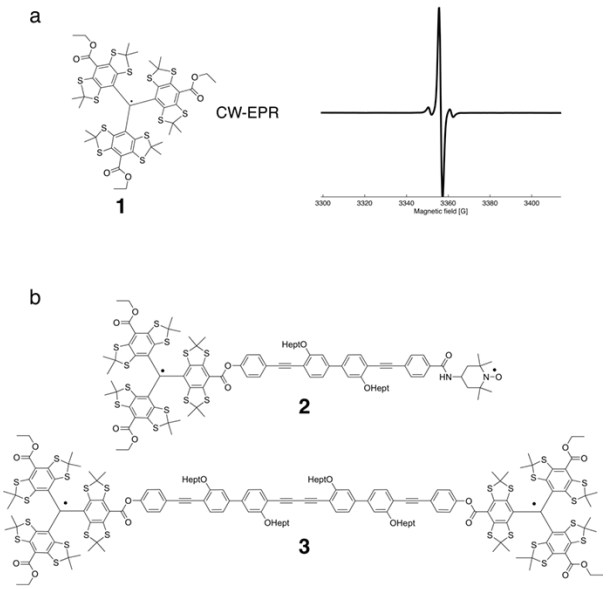

Triphenylmethyl radicals, or so-called trityl or Gomberg radicals, are persistent organic open-shell molecules with the unpaired electron being centred on carbon. The trityl derivative **1** gives rise to a very narrow EPR line (~1 G) in the solid (Figure a), slow T_M-relaxation over a wide temperature range and high biostability [1]. Compared to nitroxide radicals, which have fairly broad EPR spectra in the solid (70 G), fast relaxation times and rapid reduction in vivo, trityls can be advantageous over nitroxides as spin labels for EPR distance measurements. We have used pulsed electron-electron double resonance (PELDOR) [2,3], double quantum coherence (DQC)[4] and the single-frequency refocusing technique, (SIFTER)[5] on novel trityl-nitroxide and trityl-trityl model systems to evaluate this.

PELDOR measurements on the trityl-nitroxide biradical **2** resulted in orientation selective time traces with ~85% modulation depth compared to ~45% for bisnitroxides. Also DQC measurements using a commercial X-band spectrometer became feasible on this system, showing time traces with a well-defined modulation and a better signal to noise ratio. This is impossible for bisnitroxides.

DQC and SIFTER measurements on the trityl-trityl biradical **3** also afforded time traces with deep modulation and excellent signal to noise. The relaxation behaviour of the bis-trityl system even enabled distance measurements at 100 K (liquid nitrogen) instead of 50 K (liquid helium) needed for bisnitroxides.

This clearly demonstrates the advantages of using trityl radicals as spin labels for nanometer distance measurements and holds great promise for their application in biological systems and materials.

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[4] Borbat, P.P. *et al.*, Chemical Physics Letters (1999) 313, 145-154.
[5] Jeschke, G. *et al.*, Chemical Physics Letters (2000) 331, 243-252.

Quantum information processing with molecular nanomagnets

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The quantum spins associated with electrons and nuclei, with their discrete quantum levels and weak interactions with other degrees of freedom, offer a natural class of systems for embodying quantum information. Many possible condensed matter electron-spin-based qubits have been examined, including, for example, paramagnetic defects and bound donors in semiconductors, self-assembled and lithographically defined quantum dots, and various paramagnetic molecular systems.

High spin systems (for which $S > 1/2$) with anisotropy, such as artificial molecular nanomagnets, offer the possibility of higher density information storage and may host quantum algorithms locally. We have studied the phase coherence of spin states in nanomagnets and optimised the phase memory time by chemical engineering of the molecular structures.

Traditionally, quantum spin states are manipulated using static and resonant magnetic fields. However, electrically-controllable spin qubits would offer substantial architectural advantages for the design of a quantum information processor because electric fields may be applied over shorter length scales than magnetic fields. Certain kinds of molecular magnets, for example those exhibiting spin frustration and broken inversion symmetry in their internal structure, may be suitable candidates.

Electronic and Magnetic Properties of a Tris(hydroxo)-bridged Chromium Dimer, a Challenge for DFT

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The calculation of zero field splitting (ZFS) parameters using density functional theory (DFT) has become possible in recent years and has demonstrated a good accuracy in calculating axial splittings for single metal systems. We present work showing a current limitation of DFT when extended to a more challenging, multi-metal system and discuss the potential impact on our ability to scale computations to treating single molecule magnets. The calculation of the energy ladder of the spin states for Kremer's chromium dimer[1-3] is demonstrated to be problematic at the DFT level. Complete active space self consistent field (CASSCF) calculations provide insight into the reasons for the failure of DFT. ZFS parameters calculated at the CASSCF level are presented and validated against experiment.

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New techniques in determining the spin label orientation using high power W-Band PELDOR

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[1]School of Physics and Astronomy, Centre of Magnetic Resonance, University of St Andrews, St Andrews KY16 9SS, UK. [2]Biomedical Sciences Research Complex, Centre of Magnetic Resonance, University of St Andrews, St Andrews KY16 9ST, UK.

Recent advances in high power, high bandwidth, EPR instrumentation at W-band have made it possible to obtain accurate and highly sensitive PELDOR (Pulse Electron-Electron Double Resonance) measurements that allow both distance and orientational information to be extracted [1]. In deuterated systems it is now appears possible to measure distances substantially beyond 10nm and new rigid spin labels also now offer the potential for orientation sensitive measurements to be used systematically for the study of large supramolecular biomolecular systems [2]. However, a central challenge in the analysis of the data, is to separate out the contributions from orientational distributions and distance distributions in a computationally efficient manner.

In this paper by applying multivariate statistics and appropriate measurement techniques we show:

1) That it is possible to separate the orientation and distance information from appropriate sets of PELDOR traces at W-band.
2) For rigid systems the experimental methodology appears to give data sets that offer a unique angular solution. (within the inherent symmetries)
3) For typical measurement sets, it appears to be possible to achieve angular accuracies better than 5 degrees for rigid systems.
4) It is possible to identify sets of possible angular distributions for cases where there is more flexibility in the system.

To achieve insights into the orientation effects, simulations based on the method published by the Prisner lab have been implemented on a GPU processing platform [3]. The rapid orientation matching process uses only the orientation component of the measured data measured using the high power pulsed W band spectrometer HiPER. Comparisons of experimental and simulated data will be shown showing the potential of the technique.

1. G.W. Reginsson *et al.*, W-Band PELDOR with 1kW Microwave Power: Molecular Geometry, Flexibility and Exchange Coupling, *J. Magn. Reson.*, in press.
2. M.R. Fleissner *et al.*, Structure and dynamics of a conformationally constrained nitroxide side chain and applications in EPR spectroscopy, *Proceedings of the National Academy of Sciences*, 2011, 108, 16241-16246.
3. A. Marko *et al.*, *Journal of Chemical Physics*, 2009, 130, 064102.

From electron-nuclear spin pairs to the electron spin interaction with the bulk nuclei: a closer look at dynamic nuclear polarisation

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Techniques based on nuclear magnetic resonance (NMR) are widely used in spectroscopic and imaging applications in chemistry, physics and biological and medical sciences. The major advantage offered by these techniques is the easy identification of chemical compounds via their specific resonance lines and, particularly relevant for medical applications, the non-invasive detection of the NMR signal. The major drawback is the relatively low sensitivity of these methods under normal experimental conditions due to the weak nuclear Zeeman effect. However, it is possible to generate non-thermal nuclear spin polarisation by exploiting the coupling between electron and nuclear spin ensembles in dynamic nuclear polarisation (DNP) experiments that can provide, under certain conditions, an increase of the NMR signal by more than a factor of 10^4 in comparison to the signal arising from the thermally polarised nuclear spin ensemble. The dramatic increase in the signal can be used to accelerate conventional NMR spectroscopy experiments cutting down the experimental time from days to milliseconds or improve the sensitivity for the in vivo detection of low concentrated endogenous molecules in medical magnetic resonance imaging experiments.

I will analyse in detail the spin physics of various DNP strategies and describe several theoretical approaches to obtain realistic simulations of the spin dynamics in DNP experiments also for systems of many coupled spins. In addition I will discuss the dependence of the DNP effect on radical properties. Furthermore, I will introduce experimental implementations and describe some key applications.

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J. Leggett, R. Hunter, J. Granwehr, R. Panek, A.J. Perez-Linde, A.J. Horsewill, J. McMaster, G. Smith, W. Köckenberger (2010), *Phys. Chem. Chem. Phys*. **12(22)** 5771-5778

Techniques to improve sensitivity and capability in high field pulsed EMR experiments

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School of Physics and Astronomy, University of St Andrews, Fife Scotland
**School of Biomolecular Science, University of St Andrews, Fife Scotland*
***School of Life Sciences, University of Dundee, Scotland*

This paper will give an overview of techniques to improve the sensitivity of pulsed EPR in high magnetic fields and show that it is possible to measure high quality orientational dependent PELDOR data that allow both orientation and distance distribution information to be extracted in biomolecular samples.

Techniques to further improve sensitivity are discussed in terms of new sample holders, new pulse sequences, new sample preparations and new analysis methods. Experimental results are presented using a kW high power wideband pulsed EPR spectrometer at W-band operating with an instantaneous bandwidth of 1GHz with very low dead time with large sample volumes.

Potential extensions for pulsed EPR to higher powers and wider bandwidths are outlined.

Theoretical modelling of orientation-dependent EPR spectra in organic solar cells

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[1]Department of Materials, Imperial College London and London Centre for Nanotechnology; [2]Department of Physics and Astronomy, University College London and London Centre for Nanotechnology.

The functionality of organic thin films is strongly dependent on nanostructure and molecular orientation: e.g. charge transport, light absorption, and anisotropic magnetization. Characterisation of such complex organic nanostructures is essential for both fundamental understanding and quality control. The conventional techniques for characterization include x-ray diffraction (XRD) and near-edge x-ray absorption find structure (NEXAFS), etc. However, XRD and NEXAFS are problematic when the material is amorphous or mixed. Instead, electron paramagnetic resonance (EPR) provides an alternative route to circumvent these problems for the structural characterization of pure copper-phthalocyanine (CuPc, spin-1/2) solar cell or mixed organic solar cell that consists of CuPc and C_{60}. [1] Our theoretical modelling of EPR spectra adopts a spin Hamiltonian containing an isotropic exchange interaction between electron spins and an anisotropic hyperfine interaction between copper nuclear spin and electron spin. The EPR spectra are constructed by using Fermi's golden rule and powder-averaged according to different molecular orientations including molecular plane perpendicular and parallel to substrates. Simulations of EPR spectra are in a very good agreement with experiments qualitatively as shown in Fig. 1. The combination of theory and experiments suggests a novel and more efficient way to detect the orientation of molecules in organic solar cells, which could be useful for factories. Furthermore this work can shed light on the spin-light emitting diode (spin-LED) and spin-field effect transistor (spin-FET).

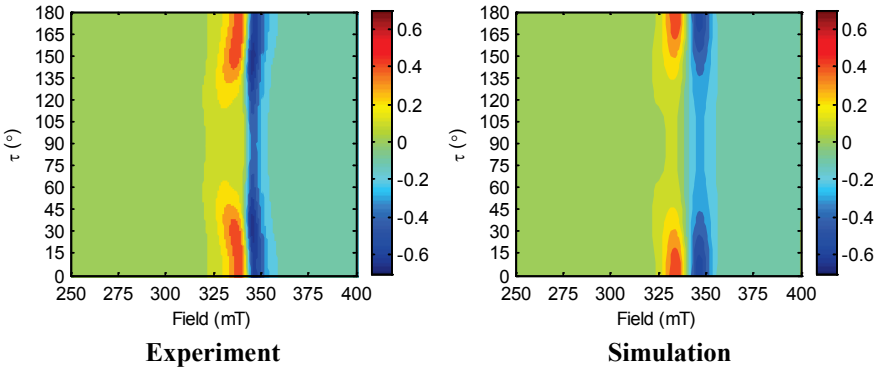

Fig. 1: a comparison between simulation and experiment for the mixture of CuPc and C_{60}. The theoretical modelling is in a good agreement with experiment and suggests that CuPc molecules are perpendicular to substrates.

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Closing the simulation loop: direct fitting of atomic coordinates of radicals to experimental ESR data

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School of Chemistry, University of Southampton, Highfield Campus, Southampton, SO17 1BJ.

We report geometric structures of several organic radicals, both in solution and in protein powders, determined by direct variation of atomic coordinates against the experimental ESR data. In the fitting procedure, we take advantage of the recently introduced large-scale spin dynamics simulation algorithms [1] and of the fact that the accuracy of quantum mechanical calculations of magnetic parameters has improved to the point of quantitative correctness – it is now possible (although still expensive from the supercomputing resource perspective) to reproduce experimental ESR spectra by varying atomic coordinates in the DFT input [2].

Solutions or workarounds are presented for the three significant difficulties encountered in such schemes – the local minimum problem in spectral fitting, the lack of vibrational averaging in the quantum mechanical calculations of magnetic parameters and the lack of analytical derivative algorithms for magnetic parameters.

For tyrosyl radicals in protein environment, the fitting runs require around 50 BFGS iterations with four-point central finite-difference *g*-tensor and hyperfine tensor gradients computed at each step for 63 coordinates – to a total of 25,200 independent GIAO B3LYP/EPR-II calculations, consuming about 10,000 core-hours on our SGI Altix 4700 supercomputer. The cost of the same number of spin dynamics simulations is much smaller. It is likely that the fitting times would be reduced once the analytical gradients of magnetic parameters become available.

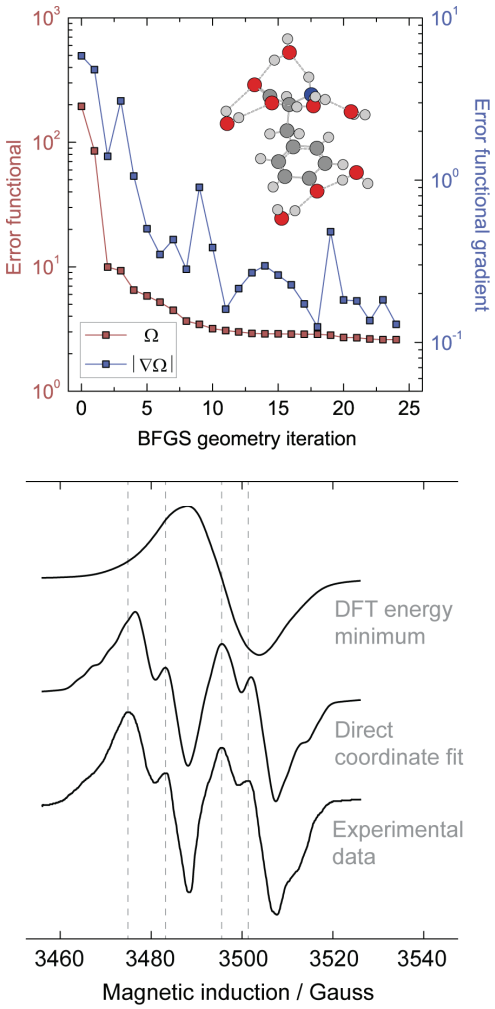

Figure 1. Upper panel: tyrosyl radical geometry convergence profile (all-atom fitting to a powder ESR spectrum in *E. coli* ribonucleotide reductase (PDB: 1RIB/Tyr122) . Lower panel: the resulting fit as compared to the spectrum computed at the DFT minimum geometry and the experimental data.

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Probing (anti)-oxidative effects with time-resolved EPR and CIDNP

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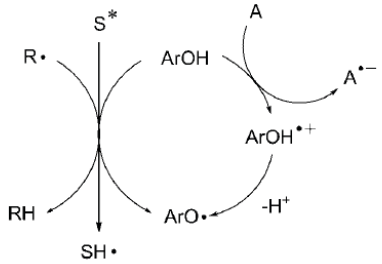
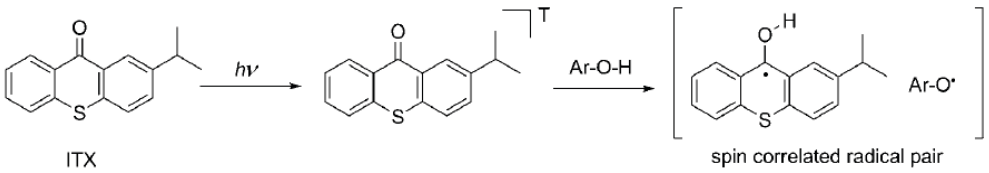
**Institute of Biochemistry, Food Science and Nutrition, Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, P.O.Box 12, Rehovot 76100, Israel.

We have followed hydrogen abstraction reactions (Scheme 1) from model polyphenols (catechin, gallocatechin, epigallocatechin, and epigallocatechin gallate) and "real" tea by using photoinduced reactions between the model compounds and tee with thioxanthone (Scheme 2) [1]. Analogous experiments were carried out to establish the reactivity of model compounds for lipid peroxidation, e.g. linoleic acid [2].

The reactivity at a 50 ns – ms time scale was established by (time-resolved) EPR and CIDNP spectroscopy.



Scheme 1. Antioxidative pathways of polyphenols



Scheme 2. H-abstraction reactions with ITX

The products formed at a 50 ns – ms time scale were established by (time-resolved) EPR and CIDNP spectroscopy.

[1] Neshchadin, D.; Levinn, R.; Gescheidt, G.; Batchelor, S. N. *Chem.-Eur. J.* **2010**, *16*, 7008-7016.
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ESR and Electrochemistry Studies on Sterically Congested R_3E (E=As,P) and R_2PPR_2

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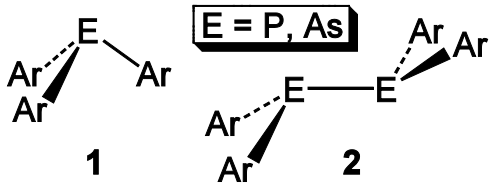
Cation radicals of trivalent organophosphanes and organoarsanes are normally extremely reactive and have commonly been observed only in low-temperature matrix studies. However, recent work has shown that bulky aryl groups can dramatically stabilize such ion radicals [1,2].



In this communication, we report on the synthesis and structure determination of novel examples of bulky triarylpnictophanes and tetraaryldipnictophanes **2**. The results of detailed studies on their one-electron and two-electron oxidations using chemical and electrochemical methods will be discussed. The use of ESR methods for the characterization of the cation radicals in mobile and rigid phases has been central to this undertaking. Significant structural changes that accompany the oxidation reactions have been examined using hybrid DFT computational methods which are used in conjunction with the ESR evidence for the structures of the radical cations.

We will comment on the scope of spectroelectrochemical methods for the study of inorganic main-group-element redox chemistry.

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Naphthoxanthenyl: An Unusually Stable Carbon-Centered Free Radical

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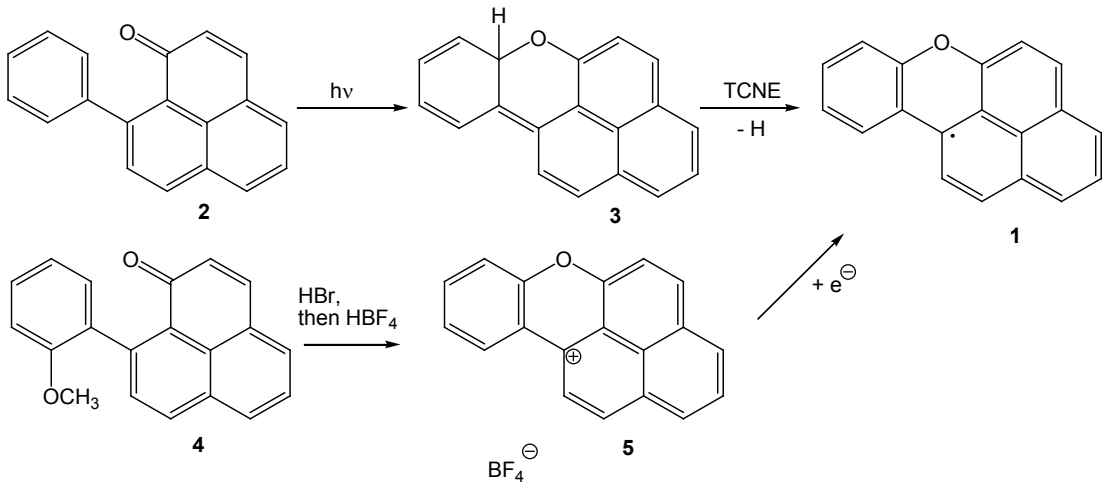
We report on the synthesis and characterisation of naphthoxanthenyl **1**, a novel carbon-centered radical. Radical **1** can be generated using two different approaches. Photocyclisation of 9-phenylphenalenone **2** results in formation of a short-lived (τ = 10 μs) reaction product **3**. Hydrogen abstraction from **3** by TCNE yields radical **1**, which can be characterised by UV/Vis and ESR spectroscopy. An independent synthesis of **1** is achieved starting from 9-(2-methoxyphenyl)phenalenone **4**, which upon treatment with HBr and counterion exchange with HBF_4 affords naphthoxanthenium tetrafluoroborate **5**. Reduction of **5** yields radical **1** as dark-green solid with bronze lustre. In the solid state, **1** shows a very broad ESR signal devoid of any hyperfine coupling. A highly resolved ESR spectrum can be recorded in dilute benzene solution. Radical **1** is persistent in solution at ambient temperature, and in the solid state and molten up to T = 230 °C, even under air.



The presentation will describe the synthesis and properties of **1**, as well as that of a series of derivatives.

Electron delocalization in multi-porphyrin systems probed by EPR

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Linear and cyclic π-conjugated multi-porphyrin systems are currently being studied for potential applications as NIR-emitters [1], molecular wires [2] and dye-sensitised solar cells, and the unpaired spin and charge delocalisation in these systems is a critical property. The electron distributions in radical cations of linear butadiyne-linked Zn porphyrin oligomers (from monomer to hexamer) and a cyclic six-membered nanoring [3] are investigated by X- and W-band EPR [4]. We aim to map out the spin density in these series of molecules by measuring the g-matrix, ^{1}H and ^{14}N hyperfine couplings and ^{14}N nuclear quadrupole couplings, with a combination of ENDOR and HYSCORE. The advantages and disadvantages of these techniques over the series of molecules will be discussed. DFT calculations will aid the interpretation of the experimental data. This talk is complementary to the poster to be given by C. E. Tait.

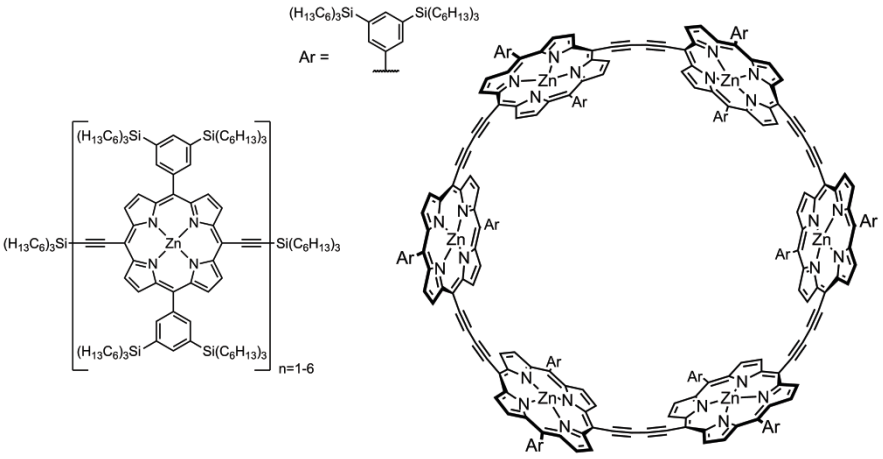

Figure 1. Structures of the oligomers and the nanoring

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Dehaloperoxidase – a Tyrosine Radical Juggler

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Dehaloperoxidase (DHP) is a bi-functional haem enzyme from the marine annelid worm *Amphitrite ornata*. DHP has a tertiary structure that is very close to that of known oxygen binding globins, such as myoglobins and haemoglobins. As such, DHP can reversibly bind oxygen. Yet in contrast to the other globins, DHP can perform a proper peroxidase function – it can use hydrogen peroxide to metabolite trihalophenols produced by other organisms of the same habitat as self defence toxins. The free radical mechanism of this peroxidase activity and the mechanism of switching between oxygen binding and peroxidation are in the focus of this study.

We have previously shown [1] that the way free radicals are formed in DHP A depends on the conformation of the distal histidine H55. When this histidine is in the most populated open conformation the radical is formed on Y34, but if H55 is in the closed conformation, it participates in the free radical transfer to another tyrosine, Y38.

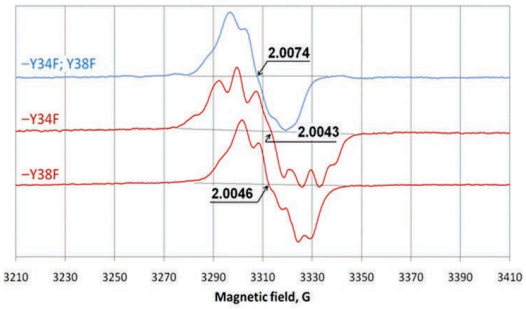

Figure 1. The free radical EPR spectra of the three DHP A mutants after reaction with H_2O_2 at pH 7.

A natural variant of DHP is DHP B which lacks Y34. We have now constructed a number of mutants of DHP A and DHP B and demonstrated how the free radical formation pathway is affected every time a tyrosine is replaced with a redox inactive residue (of a similar size and structure) phenylalanine. Two major conclusions drawn from the present work are as follows. 1) Our previous assignment of the radicals' sites in DHP A, based exclusively on the EPR spectra simulation and on the free radical kinetics is now vividly confirmed by the site directed mutagenesis. 2) The enzymatic assays of the mutants has elucidated peculiar differences in the kinetics parameters (V_{max} and K_m) which can be rationalised with the understanding of the free radical formation pattern, so strongly dependent on the tyrosines available in the enzymes' structure.

[1] Thompson, M. K., Franzen, S., Ghiladi, R. A., Reeder, B. J., and Svistunenko, D. A. (2010) Compound ES of dehaloperoxidase decays via two alternative pathways depending on the conformation of the distal histidine. *J. Am. Chem. Soc.*, **132** (49), 17501-17510.

Quantum computing on electron spins using the pulse EPR spectroscopy methodology

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I intend to discuss perspectives of quantum computing with electron spins of paramagnetic centers in solids as qubits. Potentials of the EPR spectroscopy methods to control quantum state of spins will be emphasized.

Structure and Conformational Dynamics of Nucleic Acids and Membrane Protein Complexes Studied by Site-Directed Spin Labeling

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Multi-frequency electron paramagnetic resonance (EPR) spectroscopy, different strategies of site-directed spin labeling (SDSL) and molecular dynamic simulations were combined to study the structure and conformational dynamics of nucleic acids and membrane protein complexes. Analysis of the spin label side chain mobility, its solvent accessibility, the polarity and proticity of the spin label micro-environment and inter-spin distances determined by DEER provide information for restraint modeling of molecular domains or interaction sites and their conformational changes. The presentation reviews our recent results: (i) DEER spectroscopy combined with different strategies of site-directed spin labeling was used to elucidate the conformational transition of a tetracycline aptamer upon ligand binding and the structural changes observed in mismatched or parallel DNA [1, 2]. (ii) Vinculin tail conformational changes upon binding to actin filaments and lipid membranes were studied. With this protein we also show chances and limits of orientation selection DEER at X-band frequencies [3, 4]. (iii) Light induced conformational changes of the spin labeled halobacterial phototaxis receptor sensory rhodopsin (pSRII) in complex with the receptor specific transducer (pHtrII) are shown to shift the thermodynamic equilibrium between two states of the first HAMP domain of pHtrII [5-7]. The light induced signal transfer through the protein complex could be followed by time resolved EPR experiments. Comparison of the dipolar interaction of spin labeled pSRII-pHtrII complexes reconstituted into nano-lipoprotein particles or membrane sheets reveals functional clustering of the protein complexes in the membrane sheets.

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[2] Ding P., Wunnicke D., Steinhoff H.J., Seela F. Chem Eur J 16:14385-96 **(2010)**
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[4] Abé C., Klose D., Dietrich F., Ziegler W.H., Polyhach Y., Jeschke G., Steinhoff H.-J. J Magn Reson (doi 10.1016/j.jmr.2011.12.024) **(2012)**
[5] Bordignon, E., Klare, J., Holterhues, J., Martell, S., Krasnaberski, A., Engelhard, M., Steinhoff, H.-J. Photochem. Photobiol. 83, 263–272 **(2007)**
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[7] Holterhues J., Bordignon E., Klose D., Rickert C., Klare J.P., Martell S., Li L., Engelhard M., Steinhoff H.-J. Biophys J, 100, 2275-2282 **(2011)**

Investigation of IKK Structure and Activation by site-directed spin-labeling and EPR Spectroscopy

Claire Bagnéris[*], Kacper B. Rogala[**], Vlad Zamfir[**], Benjamin Hall[***], Selina Dagless[*], Katharina F. Pirker[**], Micha B.A. Kunze[**], Tracey Barrett[*] and Christopher W.M. Kay[**]

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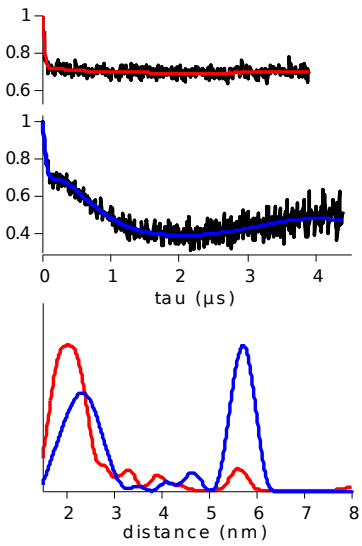
The NF-κB pathway is a prime target for lymphogenic viruses that hijack the mechanisms for proliferation through the production of host mimetic viral proteins that cannot be regulated by the existing cellular mechanisms. One such virus is Kaposi's sarcoma herpes virus (KSHV), the main causal agent of Kaposi Sarcoma (KS) which occurs most frequently in HIV-infected individuals. IKKγ, the essential modulator of the NF-κB pathway, is thought to be a homo-dimeric coiled-coil but structural data on the full-length protein (419 amino acids) is sparse as information from both X-ray crystallography and NMR are limited to short fragments. The crystal structure of the viral FLIP bound to a fragment of IKKγ [1] gave insight into the molecular basis underlying the interaction, but was unable to answer important questions concerning the conformation of IKKγ in its ground and activated states.

Nitroxide spin labels were attached to various positions in the dimeric IKKγ protein by site-directed spin labeling. Structural information about IKKγ activation by ks-vFLIP and IKKβ was obtained by a combination of cw-EPR at room temperature and DEER spectroscopy in frozen solution. The figure depicts the form factors and distance distributions obtained (using DeerAnalysis) for single pairs of labels (red) and two pairs of labels (blue). The former always give a short distance consistent with a head-to-head coiled-coil structure, whereas with two pairs of labels a long distance is also observed consistent with an extended geometry. The resulting distance information was used to model the conformation of the full-length protein in its ground and activated states for the first time.



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Investigating cyclodextrin/ PEG hydrogels properties with spin probes

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Gels are a class of soft materials capable of confining large volumes of solvent in the solid-like fibre network, which have attracted broad interest in fundamental and applied research [1]. At molecular level, gels are inhomogeneous materials and the use of spin probes in conjunction with EPR spectroscopy is a method at hand to investigate their structure and properties.

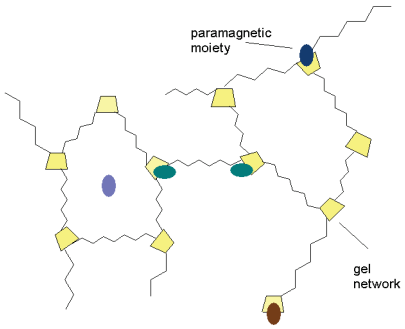

Fig 1. Schematic representation of gel network

The gel systems used in the present study consist of a covalent network formed by the reaction of isocyanate end-capped polyethylene glycol with β-cyclodextrin (CD) (Fig. 1). The gel formation was previously monitored by EPR spectroscopy [2]. In this work we aimed:

1) to investigate the influence of the polymer chain length, solvent nature and temperature on the mobility of gel network. A series of the spin-labelled gel networks have been prepared to achieve this goal.

2) to analyse the diffusion of various spin probes into the gel and the distribution between different compartments of gel (solvent pools, fibres, CD cavity). We used TEMPO and its derivatives (carboxy-TEMPO, adamantane-TEMPO) as spin probes. Due to the high affinity of the adamantane derivatives for CD cavity, adamantane-TEMPO was used to study the partitioning between gel compartments at room temperature. For the other two spin probes encapsulated in gel, information on their distribution between gel compartments was obtained from EPR spectra recorded at low temperatures (Fig. 2).

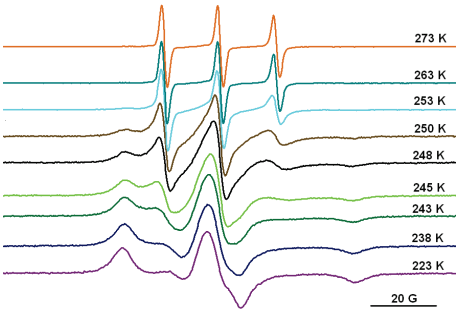

Fig 2. EPR spectra of carboxy-TEMPO encapsulated in gel

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Multifrequency Electron Paramagnetic Resonance Characterization of PpoA, a CYP450 Fusion Protein that Catalyses Fatty Acid Dioxygenation

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PpoA is a fungal dioxygenase that produces hydroxylated fatty acids involved in the regulation of the life cycle and secondary metabolism of *Aspergillus nidulans*. It was recently proposed that this novel enzyme employs two different heme domains to catalyze two separate reactions: within a heme peroxidase domain, linoleic acid is oxidized to (8*R*)-hyderoperoxyoctadecadienoic acid [(8*R*)-HPODE]; in the second reaction step (8*R*)-HPODE is isomerized within a P450 heme thiolate domain to 5,8-dihydroxyoctadecadienoic acid [1]. In the present study, pulsed EPR methods were applied to find spectroscopic evidence for the reaction mechanism, thought to involve paramagnetic intermediates. We observe EPR resonances of two distinct heme centres with *g*-values typical for Fe(III) $S = 5/2$ high-spin and Fe(III) $S = ½$ low-spin hemes. ^{14}N ENDOR spectroscopy on the $S = 5/2$ signal reveals resonances consistent with an axial histidine ligation. Reaction of PpoA with the substrate leads to the formation of an amino acid radical on the early ms time scale concomitant to a substantial reduction of the $S = 5/2$ heme signal. High-frequency EPR (95- and 180-GHz) unambiguously identifies the new radical as a tyrosyl. Further, EPR distance measurements revealed that the radical is distributed among the monomeric subunits of the tetrameric enzyme at a distance of approx. 5 nm [2].

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From radiofrequency to microwave fields: exploring the recombination kinetics of a photoinduced radical pair

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Recent experiments on a carotenoid-porphyrin-fullerene (CPF) compound have established the principle that a photochemical reaction could form the basis of the magnetic compass sensor of migratory birds [1]. Here, the effects of static, radiofrequency and microwave magnetic fields on the spin-selective recombination reactions of the radical pair derived from CPF by intramolecular photo-induced electron transfer are studied using transient absorption and time-resolved EPR spectroscopies allowing estimates of the charge recombination rates to be obtained.

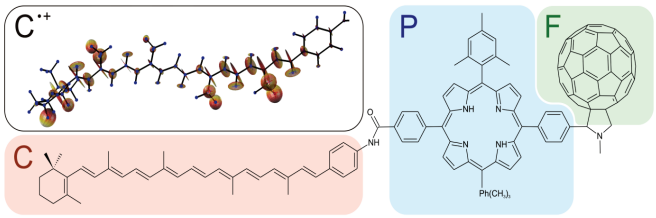

Figure 1 Structure of the CPF triad and a representation of the anisotropic hyperfine interactions of the carotenoid radical cation (inset).

Our conclusion that radical recombination must be faster from the singlet than the triplet radical pair in the temperature range studied here (110 – 200 K) is at variance with previous findings at temperatures below 90 K and above 200 K [2]. This difference may be understood in terms of the relative permittivity of the MTHF solvent which steadily increases as the temperature is lowered from 200 K and then abruptly drops back when the solution freezes (< 110 K) [3]. The increase in the relative permittivity barely affects the carotenoid triplet but causes the reorganization energy for the electron transfer to increase and stabilizes the charge-separated state resulting in a decrease in the driving force for charge recombination from both singlet and triplet states [4].

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Insight into the Electronic Structure of the Carotenoid Triplet state in Photosynthetic Proteins revealed by ESEEM and Pulse ENDOR

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The present work is a comparative investigation by pulse EPR spectroscopy on the carotenoid triplet state populated by triplet-triplet energy transfer in two different antenna proteins: the major light-harvesting complex LHCII of higher plants and the peripheral antenna Peridinin-Chlorophyll *a* Protein (PCP) from dinoflagellates [1,2].

In the light-harvesting complexes of photosynthetic organisms the presence of excess radiation can lead to photo-oxidative damage by generation of triplet state chlorophyll and subsequently singlet oxygen. The electronic properties of the carotenoid triplet states allow efficient quenching of the triplet state of chlorophyll in what is called the photoprotection mechanism. Photoprotection occurs through triplet-triplet energy transfer from chlorophyll to a carotenoid molecule via the Dexter exchange mechanism.

The structural differences between the peridinin carotenoid in PCP, which is characterized by the presence of several substituents, including an allene group and a lactone ring, and a typical carotenoid, like the lutein pigment in LHCII, could be related to different triplet state properties and consequently diverse photoprotection strategies in the two light-harvesting complexes representing opposite typologies of antenna. The aim is to recognize common features and differences in the strategy of photoprotection in terms of cofactor arrangement and electronic structure of the carotenoid triplet state.

Combining pulsed ENDOR measurements and density functional theory calculations we have derived the spin and electron densities distributions for the triplet state of both peridinin and lutein . The spectroscopic investigation on the carotenoid triplet has been focused on the effects of substituents on the electronic properties of the triplet state. Our spectroscopic findings show that despite the differences in structure and in singlet state optical properties between the highly symmetric lutein and the highly substituted peridinin molecule, the triplet states of the two molecules have unexpectedly very similar electronic structures. We have proved that the triplet-state electron density is not significantly perturbed by the presence of molecular substituents and is almost equally distributed all over the entire π-electron conjugated system. These property of the carotenoid triplet state can be interpreted as functional to guarantee an efficient photoprotection while allowing tuning of the light-harvesting properties of structurally different carotenoids.

Further insight into the electronic structure of the photoprotective site has been provided by Electron Spin Echo Envelope Modulation (ESEEM) combined with hydrogen-deuterium exchange on the PCP protein. ESEEM studies have been performed with the purpose of studying the interaction of the peridinin triplet state with a water molecule positioned at the interface between the chlorophyll and carotenoid partners involved in triplet-triplet energy transfer [1]. We have demonstrated that this water molecule is an integral part of the photoprotective system in PCP by simulation and interpretation of the experimental data in combination with state-of-the-art computational methods, suggesting a super-exchange mechanism to account for the high efficiency of the process.

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[2] Di Valentin et al., *Biochim. Biophy. Acta*, 1777 (2008) 295-307.

EPR accessibility measurements of P-glycoprotein show topography of TM6/TM12 region in different conformational states

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3. School of Biomedical Sciences, University of Nottingham, Nottingham, UK.

The multidrug efflux pump P-glycoprotein (P-gp) can confer resistance to chemotherapy of cancer through its ability to recognise an extraordinary range of substrates. This is a common feature of multidrug efflux pumps; however, the underlying mechanism remains an enigma. Topographical studies indicate a number of regions in the helices with markedly distinct physico-chemical characteristics [1-3]. These studies reveal a complex series of motions and not single fixed body alterations, highlighting the complexity of drug translocation by P-gp. The studies described characterise each of the helices independently but do not provide relative motions within the critically important region(s) of the protein. The present investigation, using electron paramagnetic resonance (EPR) spectroscopy, provides this higher resolution of information, thereby enhancing our structural understanding of micro-regions within the trans membrane domains (TMDs). It is possible to spin-label P-gp by site-directed spin-labelling (SDSL) at mutated residues 331C, 343C and 354C along transmembrane helix VI and 980C of transmembrane helix XII. EPR power saturation studies of single spin labelled mutants give us information on the local environments of these residues in different states of the protein: basal, AMP-PNP bound and ADP/Vi bound. By pair-wise spin labelling of these mutated residues we have performed initial distance measurements using the pulsed EPR technique PELDOR (pulsed electron-electron double resonance). The obtained distances and distance distributions are clearly different in different intermediate states and this structural data is used to compare the various molecular structural models available for P-gp and provides constraints for future structural studies [4].

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[4] O'Mara ML, Tieleman DP. P-glycoprotein models of the apo and ATP-bound states based on homology with Sav1866 and MalK. *FEBS Lett* **581**:4217-22 (2010).

Structure and Function of the Sodium/Proline Transporter PutP studied by EPR Spectroscopy

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***LMU Munich, Biocentre, Microbiology, Grosshaderner Str. 2-4, 82152 Planegg-Martinsried.*

PutP is an integral membrane protein located in the cytoplasmic membrane of *E. coli*, being responsible for the coupled transport of Na+ and proline. It belongs to the family of sodium solute symporters (SSSF). Structural data for PutP is yet not available, but secondary structure predictions and biochemical/biophysical analyses suggest a 13 transmembrane motif. Recently, a homology model has been developed based on the crystal structure of another member of this protein family, the Na+/galactose symporter vSGLT of *V. parahaemolyticus* [1]. Based on this homology model, previously published electron paramagnetic resonance (EPR) studies [2-4] and recent crystallographic and EPR investigations on the cognate bacterial homolog of a neurotransmitter:sodium symporter, LeuT [5], it has been proposed that helices VIII and IX as well as the interconnecting loop region eL9 determine the accessibility of the periplasmic cavities which bind sodium and proline.
We performed a cysteine scanning mutagenesis and subsequent site-directed spin labeling of eL9 in combination with EPR spectroscopy to investigate the structural features of this region and spin label mobility and polarity as well as accessibility to paramagnetic quenchers reveal inconsistencies with the present homology model, especially concerning the extent of an α-helical segment oriented approximately perpendicular to the transmembrane helices. Furthermore, our data suggest conformational changes in this region upon substrate binding including an overall motion of this helical segment that could control access to the proline binding pocket.

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[4] Hilger et al. (2009). Backbone Structure of Transmembrane Domain IX of the Na+/Proline Transporter PutP of Escherichia coli. Biophys. J. 96, 217-225.
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Using very long distance and orientation measurement to elucidate the structure of the histone Chaperone Vps75

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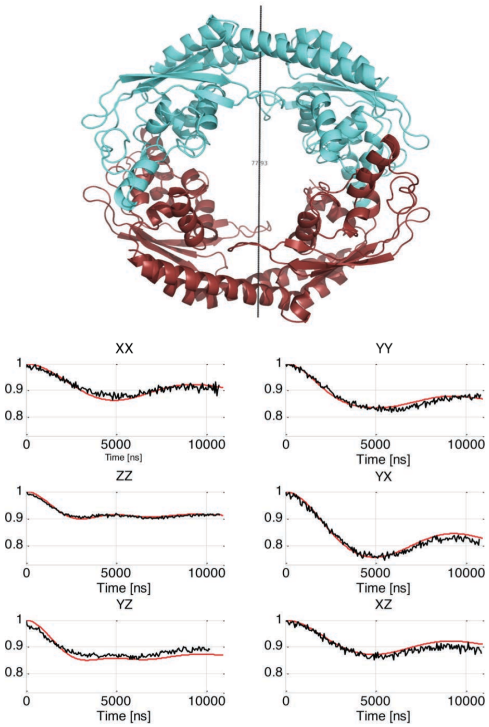
Histone chaperones are important factors in modulating chromatin structure through both direct effects on nucleosome thermodynamics and via modifications to soluble histones. Vps75 is a yeast histone chaperone that has both classical histone chaperoning functions and has a role in mediating acetylation of soluble histone H3 by the acetyl transferase Rtt109. Previous analyses of Vps75 structure using X-ray crystallography have shown it exists as a constitutive homodimer[1]. In this study we present PELDOR data, using fully deuterated protein[2], demonstrating a 76Å distance arising from a bifunctional spin label situated at the dyad axis of the homodimer. The single long distance is enough to show tetramerisation at physiological salt concentration and to define the overall tetrameric structure. Measurements at W-band and molecular dynamics simulation have been used to measure the spin label pair orientation and to apply that measurement to the refinement of the tetramer.



The tetrameric stucture defined for Vps75 is incompatible with the structures, previously defined by x-ray crystallography, for Vps75 complexed with the acetyl transferase Rtt109. We have used PELDOR to monitor the titration of spin labeled Vps75 with Rtt109. Our results demonstrate a stoichiometry of 2:1 (Vps75:Rtt109) with the conversion of tetrameric Vps75 to a dimeric form.

1) Y. Park, K. B. Sudhoff, A. J. Andrews, L. A. Stargell and K. Luger, (2008) Histone chaperone specificity in Rtt109 activation. 15, 957-964 Nat. Struct. Mol. Biol.

2) Ward, R., Bowman, A., Sozudogru, E., El-Mkami, H., Owen-Hughes, T., and Norman, D.G. (2010). EPR distance measurements in deuterated proteins. J Magn Reson *207*, 164-167.

Investigation of the intermediate state of the chaperone usher pathway in Type 1 *E.coli* using SDSL-EPR

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Bacterial infection by uropathogenic *Escherichia coli* (UPEC) is the primary cause for urinary tract infections in Europe and North America and affects many individuals; especially women. There is an increase in resistance to antibiotics by these bacteria and studies of the onset of bacterial infection are gaining importance. The active parts of the bacterium are the fibers (also called *pili*) which are assembled by the chaperone-usher (CU) pathway. The surface fiber type 1 pili are important attachment devices that target UPEC to the bladder epithelium and are encoded by the fim gene cluster (fimA-I). Type 1 pili are thus major virulence factors in the onset of cystitis.

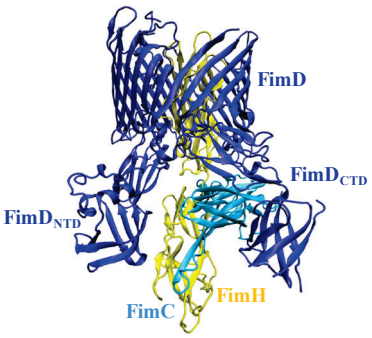

Fig 1. Crystal structure of the FimD:FimC:FimH complex in Type 1 pili of E.coli.

Recently, the crystal structure of FimD:FimC:FimH (the complex of the usher molecule FimD with the chaperone:adhesin complex FimC:FimH) was solved [1] (Fig 1). We could show using site-directed nitroxide spin labelling (SDSL) in combination with continuous wave and pulsed EPR spectroscopy that the addition of the next chaperone-subunit complex FimC:FimG binds also to the C-terminus of FimD and that the formed complex FimD:FimC:FimH:FimG is similar to FimD:FimC:FimH [1].

We are now studying the involvement of the N-terminus in the recruitment of the subunits by investigation of the intermediate state of FimD:FimC:FimH:FimG and FimD:FimC:FimH:FimF, respectively, right after the addition of the subunit FimG or FimF and before it undergoes donor-strand-exchange reaction, i.e. binding to the previous subunit FimH. Distances obtained from DEER and cw EPR measurements when the chaperone and either the N-terminal domain or the C-terminal domain was labelled, will be presented. A suggested scheme of the intermediate state is given in Fig 2.

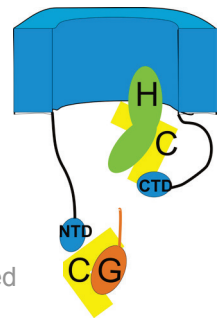

Fig 2. Proposed scheme of the intermediate state

[1] Phan et al. (2011) *Nature* 474, 49-53.

Assessing the Solution Shape and Size of Charged Dendronized Polymers Using Double Electron-Electron Resonance.

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We present double electron electron resonance (DEER) data that suggest that highly branched dendronized polymers (denpols) in solution are macromolecules with persistent shape, a well-defined envelope, and a size independent of their environment [1]. By determining the distance distribution of self-assembled dianionic spin probes (Fremy's salt dianion) on the surface of the cylindrically shaped and cationic denpols, we show that the measured solution radii are in good agreement with the solid state radii of the neutral denpol analogues. An analytic distance distribution of particles on the lateral surface of cylinders is developed for this purpose and fitted to DEER time traces:

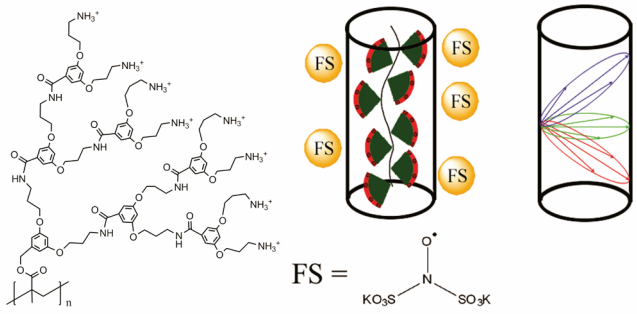

Figure 1. The molecular structure of the generation 3 denpol with the peripheral ammonium groups is shown on the left. In the center, the coordination of FS on the cylindrical surface of the dendronized polymers is shown schematically. The possible distances of a spin on the surface of a cylinder to points on the surface are sketched in the figure on the right. The red, blue and green ellipses represent only three of an infinite number of possible orientations.

$$P(r) = \frac{2r}{L^2\pi}\left(\frac{L}{R}F(\varphi|k^2) - 2\sin^{-1}(k\sin\varphi)\right)\Big|_{\varphi=\Re\cos^{-1}\left(\frac{L}{r}\right)}^{\Re\sin^{-1}(k^{-1})}$$

Therefore, DEER in combination with site-directed spin probing provides an indirect and simple method to determine the solution shape and size of macromolecules on the nanometer scale. It furthermore shows that at least generation 4 and 3 denpols in solution may already be described as molecular objects.

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Composite Pulses in W-band PELDOR experiments

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The use of composite pulses, or adiabatic pulses or so called optimal control pulses offer considerable potential in improving the sensitivity of a whole range of pulse EPR experiments, particularly at high fields and for non-resonant sample holders. In this paper we present recent results demonstrating that composite pulses can be successfully used at W-band within a highly sensitive very high power pulse spectrometer with 1 GHz instantaneous bandwidth [1].

Composite pulses have been widely used in NMR experiments since their first implementation in 1979 [2], where they can offer increased excitation bandwidth and compensate for B_1 inhomogeneity across the sample. However, their use in EPR has been limited, mainly due to the phase and amplitude distortions introduced by switches, amplifiers and the cavity, and the nanosecond time-scales required for the pulses. Recent improvements in high speed electronics now mean that many of these techniques are becoming technically viable. We describe a new type of 4-channel phase box that gives 16 programmable phases that can be switched on nanosecond timescales within a single pulse.

We experimentally demonstrate that replacing the pump pulse with a composite pulse in W-band PELDOR experiments can provide a significant improvement in both modulation depth and overall sensitivity. We also show it is possible to achieve a significant enhancement in the amplitude of the refocused echo for 4 pulse PELDOR experiments, by replacing both the 180 degree detection pulses with composite pulses.

We discuss some of the experimental challenges encountered, outline a number of techniques to improve the sensitivity further and discuss the overall potential of the technique.

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Optimal Control of Spin Dynamics in Magnetic Resonance

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Typical NMR and EPR magnetic resonance experiments consist of a series of pulses with well-defined tasks. However, due to experimental constrains (e.g. maximum B_1 amplitudes) and imperfections (e.g. B_1 field inhomogeneity) the performance of the individual pulses and of the entire pulse sequence is suboptimal in many applications. A number of new approaches have recently been developed for pulse sequence design based on powerful optimal control methods that can also take into account relaxation effects (1,2). On the one hand, individual point-to-point (PP) and universal rotation (UR) pulses can be optimized (3,4). On the other hand, entire experimental building blocks and multiple-pulse sequences can be designed (5-7).

Whereas the realization of optimized shaped or composite pulses with micro second time resolution is standard in NMR, the application of modulated pulses with nanosecond time resolution in EPR spectroscopy has only recently become possible due to the availability of fast arbitrary waveform generators (8). Experimental imperfections such as B_1 inhomogeneity and amplitude and phase transients need to be taken into account in the optimization of robust pulses for practical applications. First EPR applications include broadband excitation pulses for isolated spins and for isotropically coupled spin systems.

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Characterization of protein conformational changes with sparse spin-label distance constraints

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Distance measurements between spin labels in proteins have matured and are now applied to a multitude of problems of current interest in structural biology [1]. Many of the applications are concerned with large-scale conformational changes of proteins, which are hard to characterize with established high-resolution techniques such as x-ray crystallography and NMR spectroscopy. For this purpose, a general modelling procedure is still missing and it is often hard to assess reliability of the conclusions that are drawn from a small number of distance constraints. The problem of fitting the final conformation from a known initial conformation and distance constraints is usually underdetermined, i.e., the set of constraints is sparse.

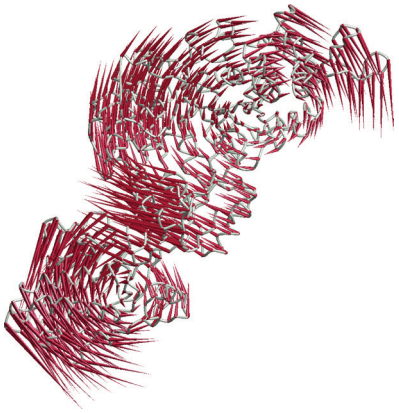

Figure 1. Motion picture of elongation factor 2 obtained with 20 label-to-label distance constraints and the Zheng/Brooks algorithm [2] (simulation).

We have examined how well conformational changes can be modelled by using a sparse set of distance constraints for driving a coarse-grained elastic network model from the initial to the final conformation. For that we have adapted the Zheng/Brooks algorithm [2] to the problem by including spin labels, whose conformations are modelled by a rotamer library approach [3]. We assume that such rotamer library modelling reduces uncertainty of the distances in the model to a standard deviation of 3 Å compared to about 7-8 Å when using them as C^{β}-C^{β} distances.

For many types of motion with more than 4 Å C^{α} root mean square deviation between the initial and final conformation and protein sizes between 100 and 1000 residues we find that separation into domains and general directions of domain motion can be recognized with 20 to 50 distance constraints, whereas the amplitude of the motion may be somewhat uncertain. Data can be interpreted by visualizations such as the one shown in Figure 1. The approach is implemented in the software MMM version 2011.1 [4].

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PELDOR in membrane proteins: potential pitfalls and loopholes

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Pulse EPR distance measurements have evolved to a standard tool for generating long-range constraints for structural modelling. Especially the pulsed electron−electron double resonance (PELDOR or DEER) [1] method is becoming increasingly applied [2,3]. Especially for structural studies on different functional states of membrane proteins which are difficult to access by most biophysical methods PELDOR is very promising.

However, in samples of membrane proteins several approximations commonly made in data analysis might not be well met. The effect of the finite concentration on the time domain data obtained is not necessarily as straightforward as in homogeneous solutions. In the latter the distribution of electron spins can be assumed to be homogeneous in three dimensions leading to an exponential decay function representing the concentration background. In phospholipid vesicle membranes this distribution might be homogeneous in lower dimensionality leading to stretched exponential functions and rather challenging signal decay times [4]. In detergent-solubilised samples it is doubted that the distribution of spin centres is homogeneous at all [5]. Furthermore, systems of singly-labelled monomers forming trimers or higher oligomers not only allow extracting the oligomerisation state from the modulation depth [6], but also exhibit multi-spin effects hampering the distance analysis [7] which are often neglected. These multi-spin effects should increase significantly with oligomeric state.

In this contribution we will address these pitfalls for data acquisition and analysis and present potential loopholes how some effects can be either avoided or properly treated in data analysis.

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DEERS – combining the sensitivity of 3p-DEER with the versatility of 4p-DEER

Lovett, J. E., Lovett, B. W., Harmer, J.

Over approximately the last fifteen years the electron paramagnetic resonance (EPR) technique of double electron electron resonance (DEER) has attracted considerable attention since it allows for the precise measurement of dipole-dipole coupling between radicals and thus can lead to distance measurements between pairs of radicals on a nanometre scale. The "deadtime free" 4-pulse DEER method has been of particular interest but can be problematic if the T_m of a system is not long enough to collect good data from the 4-pulse DEER sequence. In this paper we show that the 3-pulse sequence offers much greater sensitivity than the 4-pulse method and that this is crucial in measuring systems with a limiting T_m. We go on to show that by combining 3- and 4-pulse DEER experiments using a method coined DEER-Stitch (DEERS) accurate dipole-dipole measurements can be made which combine the sensitivity of the 3-pulse DEER sequence with the deadtime free versatility of the 4p-DEER method. To develop the DEER-Stitch method three systems were measured: a semi-rigid *bis*-nitroxide labelled nanowire, a *bis*-nitroxide labelled protein, CD55 with a distance between labels of almost 8 nm and a dimeric copper amine oxidase from *Arthrobacter globiformis* (AGAO).

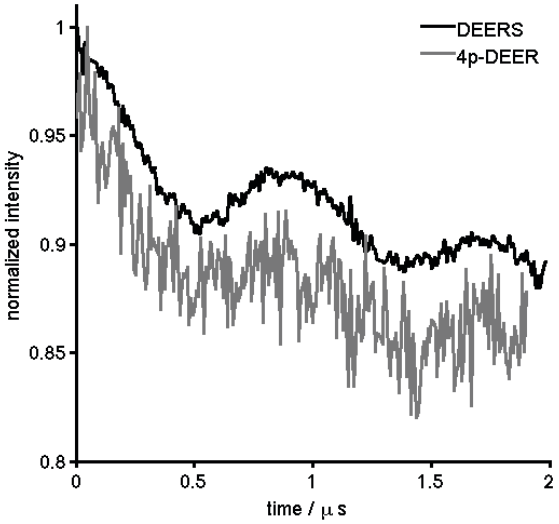

Figure: measuring the dipole-dipole interaction between pairs of copper ions in a copper amine oxidase protein using conventional 4p-DEER and by combining 3p and 4p-DEER (DEERS). The time traces were averaged a similar number of times.

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New aspects of nitroxides and open-shell graphene fragments chemistry: From quantum computers to energy conversion elements

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Recently, organic stable open-shell molecular systems have taken part in the emerging field of quantum computing and quantum information processing (QC/QIP), in spite of the fact that synthetic electron spin qubits are the latest arrival amongst many physical qubits. One of the reasons why the synthetic qubits have emerged is the capability of molecular designing for scalable electron spin qubits. Particularly, this bottom-up approach is important for the periodic assemblies of electron spin qubits such as Lloyd model for scalable quantum computers, where *g*-tensor engineering is an underlying guiding principle [1,2]. Nitroxides as typical organic stable open-shell entities can afford pilot schemes which could be extended to the QC/QIP systems with non-scalable qubits. Nitroxides have been conceived of as well-localised spin systems. The localized feature has been exploited to establish the *g*-engineering in nitroxide-based multiradicals, which allows us to execute quantum gate operations.

On the other hand, well-delocalised stable open-shell organic systems such as phenalenyls or open-shell graphene fragments [3] can afford to provide different pilot schemes in quest of new molecular functionalities in quantum terms. The schemes recently found, but dating back to the early 2000s, are relevant to tailored molecular spin devices or new types of energy conversion [4]. Interestingly, the related phenomena in the crystalline form are underlain by multi-centred bonds as a new type of chemical bonding occurring in the delocalised systems.

Spin dynamics related to spin quantum tunnelling will also be dealt with, where an organic high spin system undergoes the slowing-down relaxation due to the occurrence of phonon bottle neck phenomena at low temperature. In addition, double quantum transitions appearing in the fine-structure ESR spectra from a stable nitroxide-based triplet biradical with a sizable *D* value will be discussed on the basis of electron spin transient nutation spectroscopy.

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EPR study of the mobility of nitroxide radicals confined in MIL-53(Al) nanochannel system

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** *Boreskov Institute of Catalysis, Russia.*

Recently, micro and meso-porous materials have attracted much attention in science due to their high practical importance in industry and medicine. Metal-organic frameworks (MOFs) exhibit the most unique and outstanding properties among porous materials, but still they are the least investigated. Study of molecular mobility of probe molecules confined in such systems could be a valuable source of information about these materials.

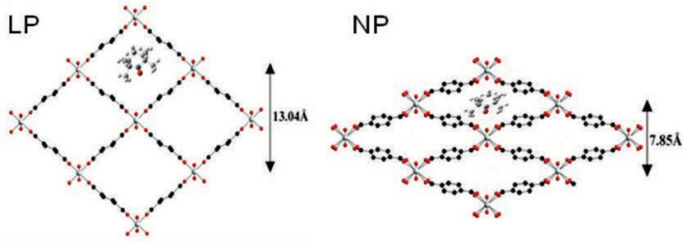

Figure 1. Structure of MIL-53(Al) in LP and NP state.

A remarkable feature of some MOFs is their flexibility. The MIL-53 type is one of the best representatives of the "breathing" MOFs (Figure 1). Depending on the guest entrapped in the pores and temperature, MIL-53 exhibits different crystalline large-pore (LP) or narrow-pore (NP) states. ^{2}H NMR spectroscopy [1], CW and pulse EPR spectroscopy [2] are reliable tools to extract information about dynamics of molecules confined in porous media.

In the present research we examined the molecular motion and orientation of several probe molecules such as TEMPO, hexamethyl imidazolidine, di-*tert*-butylnitroxide in the MIL-53(Al) nanochannels. Temperature dependence of the CW EPR and Echo-Detected EPR spectra (9/34 GHz) was measured in the polycrystalline sample of MIL-53(Al)/(probe molecule) with 1/1000 ratio of probe molecules per unit cell of MIL-53(Al). The effects of the molecular motion on the CW EPR line shape were elucidated using the MOMD model. The latter in conjunction with Q-band relaxation data gives reasons to assume the existence of H-bonding of probe molecules with OH groups of the MIL-53(Al) structure. It was found that the motion of all three nitroxides is more restricted in NP crystalline state than in LP crystalline state. It was also demonstrated that after heating of the sample to 400 K (temperature of transition to LP state) effect of transformation of crystalline structure into NP state cannot be detected, even after cooling of the sample in liquid nitrogen (temperature of transition to NP state is 150 K). Thus, the study of cooperative influence of the guest nitroxide probes on this transformation in MIL-53 pores is topical and currently underway.

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Multifrequency EPR of Mn^{2+} in II-VI semiconductor nanocrystals

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There is a wealth of information which becomes available from the accurate determination of the spin Hamiltonian (SH) parameters of isolated Mn^{2+} impurity ions in II-VI semiconductor nanocrystals (NCs). Such information concerns the localization of the Mn^{2+} in the volume or on the surface of the NCs, their ground state properties, as well as the structural and chemical changes undergone by the NCs under various thermo-chemical treatments.

Here we present a procedure, illustrated with a few examples, for determining with high accuracy the SH parameters of Mn^{2+} in ZnS and ZnO NCs, based on the analysis of multifrequency EPR spectra with line shape simulation and fitting computing programs, including the hyperfine forbidden transitions and large line broadening effects [1].

The analysis of the Mn^{2+} EPR spectra in small (~ 2 nm) cubic ZnS NCs (Figure 1) resulted in the determination of the preferred substitutional localization of the Mn^{2+} in the NCs volume at Zn^{2+} sites perturbed by a neighbouring extended lattice defect [2], as well as the identification of the different paramagnetic centres associated to the Mn^{2+} ions localized on the ZnS NCs surface, formed under various thermo-chemical treatments [3].

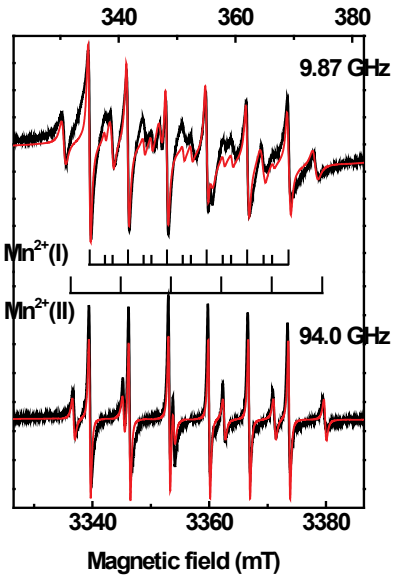

Figure 1. Experimental and simulated EPR spectra of Mn^{2+} centres in cubic ZnS nanocrystals.

We have also identified the Mn^{2+} centres in nanostructured hydrozincite and observed its thermal decomposition into ZnO. A careful analysis of the Mn^{2+} spectra allowed us to monitor the lattice ordering in the resulting ZnO NCs submitted to further annealing [4].

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EPR in bioenergetics and photovoltaic research

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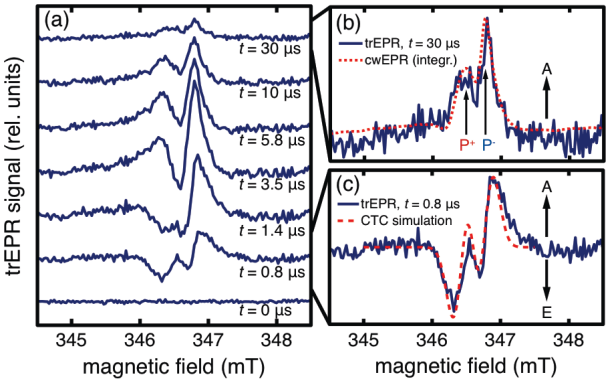
Paramagnetic states are key intermediates in energy conversion processes and are ideally analysed by EPR techniques. Here we report on studies in bioenergetics and photovoltaics. Photoinduced charge transfer and subsequent charge separation are the key processes in organic solar cells. Prior to exciton separation into free charge carriers, bound polaron pairs (also referred to as charge-transfer complexes, CTC) form at the donor/acceptor interface. While the existence of CTC was confirmed by optical spectroscopy and electrical measurements, their exact role in the process of free charge carrier generation is subject to ongoing discussions. The description of the CTC is in complete analogy to spin-correlated radical pair states well known in EPR on photosynthetic reaction centres. Transient EPR (trEPR) measurements with sub-µs time resolution performed on a P3HT:PCBM blend at low temperatures yield immediately after photoexcitation spectra with signatures of spin-correlated polaron pairs [1]. These spectra decisively differ from the spectrum of separate polarons commonly observed in light-induced cwEPR. The pair partners (positive polarons in P3HT and negative polarons in PCBM) can be identified by their characteristic *g*-values. The fact that the polaron pair states exhibit strong non-Boltzmann population unambiguously shows that both constituents of each pair originate from the same exciton. We demonstrate that coupled polaron pairs are present even several microseconds after the initial charge transfer step and discuss their role in mediating the conversion from excitons into separate charge carriers as probed by trEPR.



Furthermore, we will discuss EPR and ENDOR studies on complex metal centres in bioenergetics. The examples are advances in the interpretation of ^{55}Mn-ENDOR on the S_2-state of the Mn_4Ca water oxidizing complex in photosytem II single crystals, and recent studies on the unique 4Fe3S cluster in oxygen tolerant hydrogenases.

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Nature of the Fe-N bond in the reversibly superoxidized proximal [4Fe-3S] cluster of O_2-tolerant [NiFe]-hydrogenases as revealed by HYSCORE

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Oxygen-tolerant [NiFe]-hydrogenases contain a highly unusual [4Fe-3S] cluster proximal to the active site,[1-3] that can undergo two rapid and consecutive one-electron transfers.[4] Construction of a variant of O_2-tolerant *E. coli* Hydrogenase-1, in which the medial [3Fe-4S] cluster has been converted to an EPR-silent [4Fe-4S] cluster, simplifies the EPR spectrum and leads to unambiguous assignment of a strongly coupled nitrogen to one of the Fe atoms (Fe_4) of the 'superoxidized' proximal [4Fe-3S] cluster *via* HYSCORE (Fig. 1). A hyperfine coupling of A = [2.8 4.6 3.5]±0.3 MHz and nuclear quadrupole interaction $|e^2qQ|/h$ = 1.0+0.25 MHz ($\eta = 0$) for $^{14}N_{C20}$ was determined from analyses of HYSCORE spectra based on a S = ½ and I = 1 system with consideration of J coupling. The results provide compelling experimental support to the proposal that the 'superoxidized' $[4Fe\text{-}3S]^{5+}$ cluster contains a valence-localized Fe_4^{3+}-N bond,[1,2] recruiting the backbone peptide-N of cysteine-20 and enabling it to provide, very rapidly, not one but *two* electrons, to ensure full reduction of the O_2 molecule when it attacks the active site during H_2 oxidation.

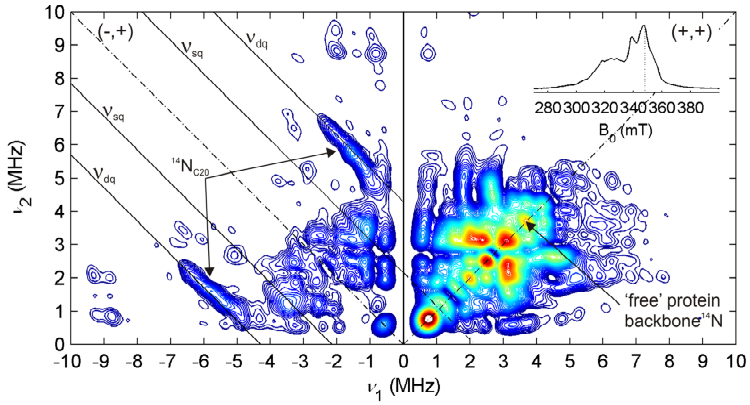

Figure 1 X-band HYSCORE spectrum showing the strongly coupled ^{14}N nucleus observed in *E. coli* Hydrogenase-1 at high potential.

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Cryptochromes: Potential compass molecules with an unexpected variety of electron transfer pathways

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Cryptochromes (Cry) form, together with their siblings, the photolyases (PHR), a divergent protein family occurring in all three kingdoms of life. Whereas PHRs repair specific UV-induced DNA damages, the Crys' functions are diverse ranging from controlling plant growth and development and entraining the circadian clock to being the candidate magnetoreceptor in, but not restricted to, migratory birds. PHRs are well-known to readily form radical pairs (RP) between flavin (FAD) and a tryptophan (Trp) upon illumination with blue light if starting from fully oxidised FAD. In analogy, this reaction is discussed as main primary photoreaction in Crys, and it is these RPs that are at the heart of the postulated magnetoreception capabilities of those proteins.

Using time-resolved EPR (TREPR) on a Cry from *Xenopus laevis*, we could for the first time demonstrate that Crys indeed form spin-correlated RPs between FAD and Trp upon blue-light illumination [1], a necessary but not sufficient prerequisite for being a magnetoreceptor. Additionally, we assigned the RP partners and showed that the magnetic coupling parameters of these RPs are in favour of sensing even weak magnetic fields such as the Earth's, as previously discussed theoretically [2]. Furthermore, with a multi-frequency TREPR approach (X- and Q-band) we could unequivocally demonstrate the formed spin-correlated RPs to originate from a pure singlet-precursor state [3].

Turning to another Cry, from *Synechocystis* sp., revealed a striking diversity in electron transfer (ET) pathways in Crys [4]: Although the conserved ET chain of three Trps (TrpA to C), common to most PHRs and Crys, is clearly present, instead of the terminal TrpC an alternative TrpC' that is further apart from TrpB than TrpC gets used as final electron donor, as we showed by applying TREPR to wild-type and mutant proteins [4].

Finally, we could show that blocking the ET pathway in *X. laevis* Cry at the first or second position (TrpA or TrpB) leads to another alternative ET involving two tyrosines (Tyr). Here, we could show that TREPR even at X-band can clearly distinguish between FAD-Trp and FAD-Tyr RPs. Taken together, these results reveal an unexpected diversity in ET pathways in Crys and show that EPR is clearly suited to investigating it.

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Following the mobility changes of G22R1 MscL upon opening and closing of the channel

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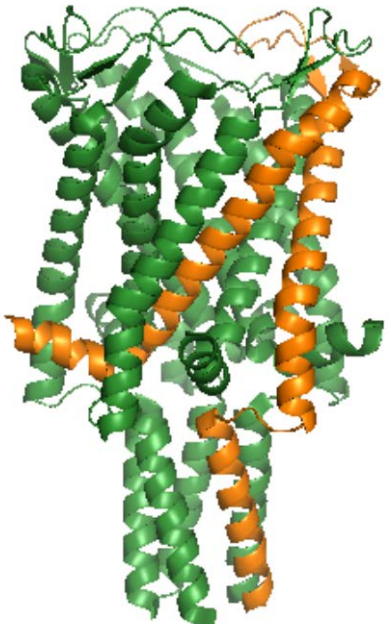
Bacterial cells are protected from the life threatening risks of hypo-osmotic shock by a family of membrane spanning **M**echano**s**ensitive (MS) channels. One of the best characterized MS channels is **M**echano**S**ensitive **C**hannel of **L**arge conductance (MscL) from Esherichia coli. Its sequence, structure from a homologue (*Figure*) and electrophysiological characteristics are well known. If cell faces sudden hypo-osmotic stress, water enters into the cells and the turgor pressure increases. MscL senses the resulting changes in the physical properties of the lipid bilayer and acts as a safety valve. It undergoes significant structural changes and opens one of the largest pores in nature – allowing passage of water, ions and even small protein molecules. Thus, MscL (and MS channels in general) is able to convert the mechanical force directly into helical movements. Even though a model of MscL opening exists, the real mechanism is still unknown.



Crystal structure of Mycobacterium tuberculosis MscL

Here, we present a method to follow helical movements of the channel towards gaining insight into the gating mechanism of MscL. We follow the structural rearrangements of reconstituted MscL by activating (and deactivating) the channel by external addition of different **L**-α-lyso**p**hosphatidyl**c**holine (LPC) concentrations and, trapping the channel in semi-closed, intermediate and open states. Deactivation is achieved by the addition of bovine serum albumin (BSA). Our strategy cobines Site-Directed Spin Labelling mutagenesis together with EPR spectroscopy and florescence dequenching assay. By labelling with (1-oxyl-2,2,5,5-tetramethylpyrroline-3-methyl)-methanethiosulfonate (MTSSL) Cys-MscL mutant in the narrowest part of the channel (G22R1), we use the changes in mobility and accessibility of R1 as a detector for the structural rearrangements of the pore-segment.

Stable (poly)radicals in supramolecular architectures and materials

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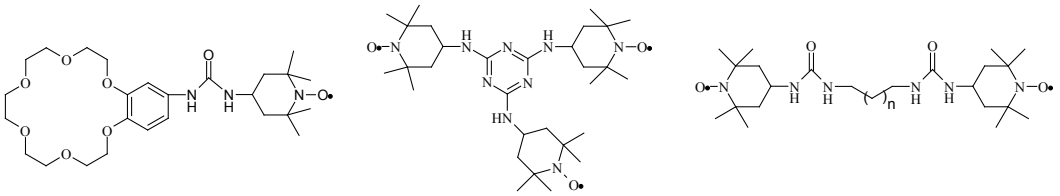
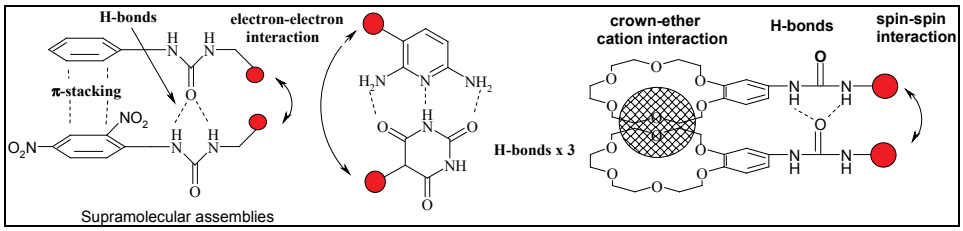
Stable (poly)radicals containing moieties able to form supramolecular bonds were synthesised and fully characterized by different means. In order to obtain supramolecular architectures and materials, the chemical design is based on non-covalent linking of individual molecules containing a free radical moiety, in such a manner that the distances between the two radical groups (spins) can be varied as desired.





Evaluation of the physical and chemical properties (electronic, magnetic, etc.) of the molecules and their supramolecular architectures, together with the possible applications as tunable organic magnetic materials, quantum electronic devices, markers and sensors, is the last target.

Elliptical overmoded cavities for High Field Pulsed DNP, EDMR and EPR applications

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School of Physics and Astronomy, University of St Andrews, Fife Scotland

We discuss and experimentally demonstrate the use of highly overmoded elliptical "integrating" cavities for extremely wideband pulse EPR, DNP and EDMR for high volume, low loss, samples at high magnetic fields.

In most pulse EPR experiments the cavity is chosen to operate with a single-mode and at low frequencies the Q is often artificially reduced to increase the available instantaneous bandwidth. Conventional wisdom has always been that there is little benefit to going to larger cavities with higher Q's, as both the bandwidth and the filling factor will reduce, and sensitivity to phase noise will increase, negating any potential sensitivity gain. It also becomes possible to excite unsuitable cavity modes that do not have optimal B_1 profiles over the sample complicating the experimental setup procedure.

However, there are a number of pulse EPR and DNP experiments where a wide-band highly overmoded approach is potentially useful at high frequencies. If the cavity becomes very large compared to the wavelength, the mode spacing can become small enough that it is possible to effectively excite a continuum of modes with a given pulse. In this case, the effective bandwidth can become extremely large. Elliptical cavities also have the nice property that the majority of cavity modes have strong field maxima centred at the two focal points of the cavity, where samples can be placed. Such experimental setups become particularly appropriate for DNP applications, where there is a requirement to have a relatively large sample volume that is uniformly excited with a large B_1 field, but where it is not necessary to detect an EPR signal with high sensitivity. The cavity can then be setup as an "integrating cavity" similar to the type used in wideband high frequency detectors. This approach potentially maximises instantaneous bandwidth, maximises sample volume and maximises the B_1 field over the sample (for a given dielectric loss).

In this paper, these potential advantages are evaluated theoretically and experimental results are presented at W-band.

An investigation into a novel flavin and fd virus chemical compass system

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Interest in chemical compass systems has long been fuelled by their speculated role in the ability of birds, and other organisms, to navigate in the earth's magnetic field [1]. To date, one chemical compass system has been found to satisfy the requirement for sufficient sensitivity to the strength and inclination of the magnetic field- the CPF (carotenoid porphyrin fullerene) triad [2]. The CPF triad compass system operates under highly unphysiological conditions; but, other chemical compass systems have remained elusive.

In this communication we propose a potential novel chemical compass system based on the flavin and fd virus system. The fd virus has the properties of a thermotropic LC (liquid crystal)- that being of a concentration dependence, as well as a non-monotonic temperature dependence, on the mesophase adopted [3]. It is hypothesised that in this compass system photoexcited flavin molecules undergo an electron transfer with certain surface accessible amino acids (eg. tyrosine) on the fd virus, to form SCRPs (spin-correlated radical pairs). The kinetics of this process may have a magnetic field dependence and we believe that with the alignment capability of the fd virus LC system, this may be translated into an anisotropic, inclination dependence. We have probed the behaviour of this chemical compass system using TA (transient absorption) and BBCEAS (broadband cavity enhanced absorption spectroscopy).

Future directions in this research may involve chemical modification of the fd virus system so as to improve the efficiency of the electron transfer between fd virus and photoexcited flavin.

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Tracing the transient conformational signal in bacterial phototaxis using SDSL-EPR spectroscopy

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In microbial photo- and chemotaxis a two-component signaling cascade mediates a regulated response of the flagellar motor to environmental conditions. Upon activation, photo- and chemoreceptors transfer a signal across the plasma membrane to activate the histidine kinase CheA. Successive regulation of the CheY-phosphorylation level controls the flagellar motor.
In *Natronomonas pharaonis* a sensory rhodopsin II – transducer complex (SRII/HtrII) mediates negative phototaxis.[1] As the initial signal, a light-induced outward movement of receptor helix F leads to a conformational change of transducer helix TM2, which in turn propagates the signal to the adjacent HAMP domain.[1,2]
For the HAMP domain, a widely abundant signaling module, several mechanisms were suggested[3], all comprising two distinct conformational states of the HAMP domain. The two states can be observed by two-component cw-EPR spectra at ambient temperatures existing in a thermodynamic equilibrium which can be driven by salt-, temperature- and pH-changes.[4]
To trace the conformational signal and it's propagation throughout the elongated transducer, we applied cw- and pulse-EPR spectroscopy in conjunction with nitroxide spin labeling. We follow transient changes by time-resolved cw-EPR spectroscopy and compare the resulting spectral changes to difference spectra corresponding to the above shifts in the thermodynamic equilibrium. The light-driven conformational changes are in agreement with a shift towards a more compact state of the HAMP domain.
Following this signal beyond the HAMP domain requires a mechanism compatible with the formation of trimers of SRII/HtrII dimers which activate CheA. An activation scheme within the framework of hexagonal arrays formed by the trimers of SRII/HtrII will be the key step to understanding the enormous cooperativity leading to signal amplification in networks formed by clusters of interacting receptors.

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presently: [#]née Döbber; [‡]ETH Zürich

EMR of La^{3+} in donor-doped $PbTiO_3$ single crystals

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Numerous examples of acceptor ion doping in a perovskite oxide, ABO_3, materials exist where electron magnetic resonance (EMR) has provide detailed information on the local structure of the centres. However, there are very few examples of EMR on donor doped systems, these have been restricted to studies of A-site substituted Gd^{3+} [1, 2]. Donor dopants have a valence greater than the ion they replace; La^{3+} substituted at the A-site, or Nb^{5+} substituted at the B-site, are the two most widely used. However, no paramagnetic centres have been observed in these systems.

Here we study the La doped crystals of $PbTiO_3$, and observe two paramagnetic centres (g = 1.978, g = 1.955) at low temperature generated by 407 nm illumination. The appearance of the signal after light illumination suggests the La incorporates in the crystal lattice as a diamagnetic state. The results of CW and pulsed EPR, and preliminary pulsed ENDOR, at X- and Q-band are presented. Superhyperfine interactions with neighbour ^{207}Pb nuclei are clearly resolved for the g = 1.978 centre.

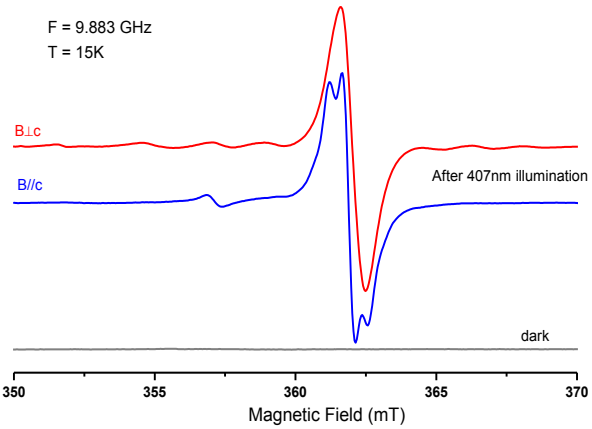

Figure 1. X-band EPR spectrum of $PbTiO_3$:La before and after 407 nm illumination at 15 K.

I.A. and D.J.K. acknowledge support from EPSRC EP/F039034/1.

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[2] R. A. Eichel *et al.*, Appl. Phys. Lett. **88**, 122506 (2006).

Pulse EPR on the iron-sulfur clusters of the membrane-bound hydrogenase from *Ralstonia eutropha*

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Resolving the problem of electrical energy generation and storage by renewable processes is one of the most important tasks today. Besides harvesting solar energy, the conversion to molecular hydrogen for storage is a promising route.
Nature has given examples of efficiently using hydrogen for energy conversion with hydrogenases. Particularly interesting are the oxygen-tolerant [Ni-Fe]-hydrogenases as they are able to metabolize H_2 at ambient oxygen levels.
The recently published crystal structure of the membrane-bound hydrogenase (MBH) of the Knallgas bacterium *Ralstonia eutropha* has revealed a novel type of a [4Fe-3S] iron-sulfur cluster in the electron transfer chain of the protein with an unusual binding motif [1]. This iron-sulfur cluster is assumed to serve as an electronic switch accepting electrons upon H_2 oxidation and delivering them when O_2 attacks the protein.

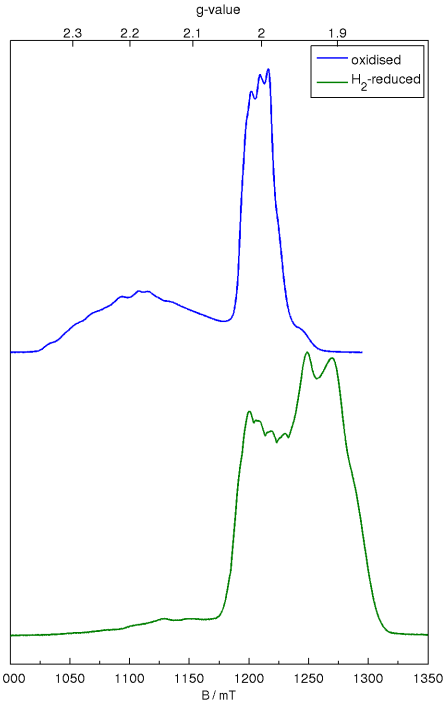

Figure 1. Q-band field-swept echo spectra of MBH in the oxidised and reduced state

Since many intermediate redox states of both the active [NiFe] site and the iron-sulfur clusters are paramagnetic, EPR spectroscopy is the method of choice for their investigation. EPR and FTIR studies have shown that the electronic structure of the catalytic [NiFe]-centre in MBH from *R. eutropha* is virtually identical to standard hydrogenases [2,3]. Here we report on pulsed EPR investigations of the novel iron-sulfur cluster in MBH in different redox states.

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Kinetics of the radiation-induced radicals of sodium tartrate dihydrate

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Radiation effects on sodium tartrate dihydrate (NaTA) were explored through a detailed electron spin resonance (ESR) study performed at various temperatures. Irradiated NaTA was observed to exhibit an ESR spectrum consisting of one main strong line and many weak lines located at both side of the main ESR line. An evaluation technique based on the variations of the characteristic resonance line intensities and the spectrum area under different experimental conditions was adopted, to determine the kinetic and dosimetric features of radical species responsible for the observed experimental ESR spectrum.

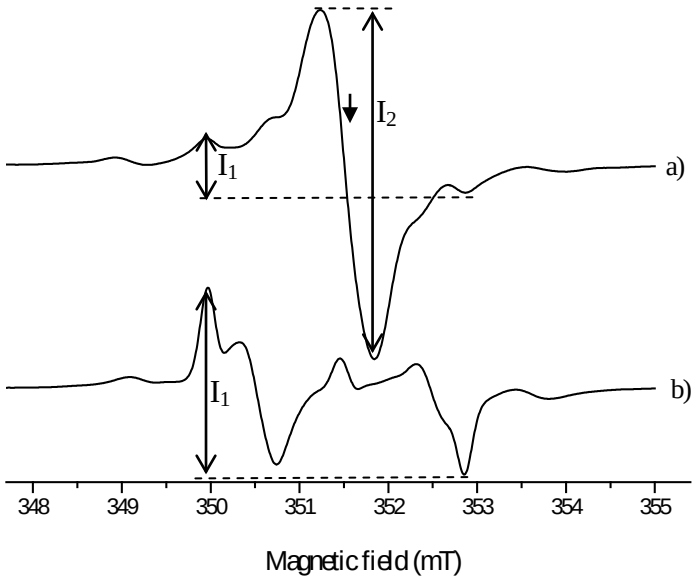

Figure 1. ESR spectra of NaTA. a) irradiated at 10 kGy, b) annealed at 335 K for 1 h. Arrow indicates the position of the DPPH resonance line (g = 2.0036).

It is found that while the total radical numbers were almost unchanged, the radical responsible for the main strong line decay to the radical that responsible for the weak lines. Thus, while the signal intensity of the main line decreases, the intensities of the weak lines start to increase after annealing the sample at high temperature (Figure 1). The similar variations of the signal intensities and transformation-generation behavior of the radicals were found, and only 25 percent of the total numbers of the radicals were decayed after three months of storage [1]. The similar transformation were reported in the literature for the radicals of tartaric acid [2-5].

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Acknowledgements: the authors want to thank for the financial support to the Turkish Research Council (TUBITAK), grant no: 110T825.

The Electronic Structure of the Lutin Triplet State in LHC-II

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Carotenoids are cornerstones of oxygenic life. In the photosynthetic apparatus they protect the cell from the photo-oxidative damage induced by light-stress conditions. Within each complex, efficient transfer of triplets from chlorophyll to carotenoids occurs as a protection mechanism against singlet oxygen formation. The triplet-triplet energy transfer process is strongly dependent on the electronic properties of the triplet states involved.

This contribution presents a pulsed ENDOR study on the triplet state of the photoprotective carotenoid – lutin - present in light-harvesting complex II (LHC-II) from *Spinacia oleracea*. ENDOR spectroscopy gives access to magnitude and sign of hyperfine slitting components along all the *Zero Field Splitting* axes. The number and the magnitude of the experimental hyperfine coupling components indicate that triplet state exciton is localized on the lutein molecule and it is not shared with neighbouring chlorophyll molecules. DFT calculations allow complete assignment of the hyperfine coupling components. The spectroscopic behaviour of lutein is compare with that of peridinin present in PCP (peridin – chlorophyll *a* – protein form *Amphidinium carterae*). The photo-protective pathway is similar in the two proteins even though the chemical structures of the carotenoids involved are very different. ENDOR data and DFT calculations clearly show that both carotenoids share the same triplet state electronic structure with the unpaired electrons uniformly delocalized over the whole π-conjugated system in an alternating even-odd pattern. This is a remarkable result considering that peridin is a highly substituted molecule and that its singlet spectroscopic properties are strongly influenced by its chemical substituents.

EPR investigation of a novel Copper Metal Organic Framework

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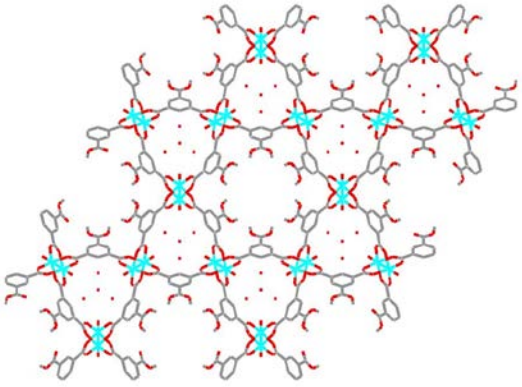
Porous materials have attracted a considerable attention over the past few decades because of their number of applications which have a direct impact on our quotidian life. They constitute potential candidates for gas storage, separation by selective adsorption, catalysis and drug storage and delivery. The most important and highly studied of these materials is the 3-dimensional HKUST-1 system which is a Copper (II) MOF where the copper dinuclear so-called "paddele wheel" building unit is connected by BTC (benzene-1,3,5-tricarboxylic acid) linkers to form a cubic MOF [1]. The commonly solvent used for the HKUST-1 preparation is ethanol and changing the system solvent to mixture methanol/water (50:50) leads to a new 2-dimensional material, which was named STAM-1 (At-Andrews MOF-1), with unique properties [2]. Initial EPR experiments on STAM-1 showed a strong signal indicating the presence of Cu^{2+} monomers, usually known as residual extraframework paramagnetic species. The presence of such species could affect significantly the properties of STAM-1, in particular the magnetic properties, and therefore a detailed investigations are needed to get a better understanding in order to elucidate their nature and to have more insight about their structure and coordination. The present study combines CW and Pulse EPR spectroscopy to explore either these extraframework species are part of the MOF's framework or are free species in the pores, and to check if they can be altered without affecting the framework structure.

Copper MOF STAM-1 Structure [2]



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Molecular Spin Clusters for Quantum Information Processing

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

Currently, there is interest in the development of molecular-scale devices for uses in quantum information processing.[1] With this application in mind, physical studies on antiferromagnetically coupled $[Cr_7MF_3(Etglu)(O_2C^tBu)_{15}(phpy)]$ molecular wheels, where M is a divalent metal cation (M = Mn^{2+}, Zn^{2+}, Ni^{2+}) have been pursued.[2] The heterometallic wheels contain an octagon of metal centres, which are bridged by fluoride ions, pivalate groups and a chiral *N*-ethyl-*D*-glucamine molecule which is penta-deprotonated and bound to the metal sites through all available O-donors. They are deep purple in colour and they have been named purple-Cr_7M. There is antiferromagnetic coupling between adjacent metal centres, $J \approx -8$ cm^{-1}, resulting in a non-zero net spin ground state.

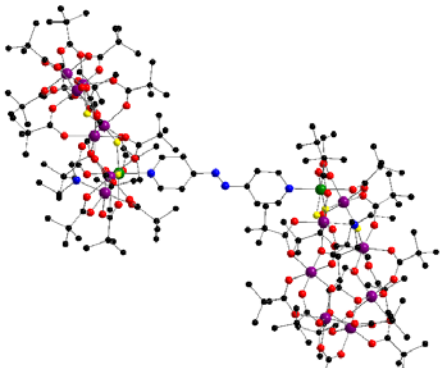

Figure 1. $[\{Cr_7NiF_3(Etglu)(O_2C^tBu)_{15}\}_2(pyN{=}Npy)]$. Colours; Cr atoms: purple; Ni atom: green; C atoms: black; F atoms: yellow; N atoms: blue; O atoms: red. All H atoms have been removed for clarity.

At the heterometal site of purple-Cr_7M wheels there is a terminal ligand which can be substituted for a variety of N-donor organic ligands. A series of bidentate N-donor linkers has been used to link Cr_7Ni wheels (each wheel $S_{eff} = {}^1/_2$) to create prototype two-qubit systems.[3] For example, $[\{Cr_7NiF_3(Etglu)(O_2C^tBu)_{15}\}_2(pyN{=}Npy)]$ (Figure 1) is a dimer of Cr_7Ni molecular wheels. The two Cr_7Ni wheels are linked via 4,4'-azopyridine, which coordinates to the Ni^{2+} site of each wheel. Multi-frequency EPR spectroscopy and SQUID magnetometry has been used to extract the spin-Hamiltonian parameters of this family. It has been shown that the single wheels can be linked together electronically as well as chemically. It has been found that for the unsaturated linkers, there is a weaker interaction between Cr_7Ni wheels when longer linkers are used. The strength of interaction is smaller for the saturated linkers than for the unsaturated linkers.

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Parallel density matrix propagation in spin dynamics simulations

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Abstract

It is well known [2] that as the number of spins in a simulation increases, the time required for the simulation rapidly becomes intractable.

Parallel computation provides a means to reduce the time required [1], but the double-sided propagation of the density-matrix, $\hat{\rho} \in \mathbb{C}^{N\times N}$, under the propagator $\mathrm{e}^{-\mathrm{i}\hat{H}t}$ (i.e. $\hat{\rho}(t+\Delta t) = \mathrm{e}^{-\mathrm{i}\hat{H}\Delta t}\hat{\rho}(t)\mathrm{e}^{\mathrm{i}\hat{H}\Delta t}$) is not obviously parallelizable.

Such an equation may be parallelized, however, if one decomposes the density matrix into the sum of the products of two vectors, i.e.

$$\hat{\rho}(t) = \sum_{n=0}^{N-1} w_n(u_n(t) \otimes v_n^{\dagger}(t))$$

where $w_n \in \mathbb{C}$ and $u_n(t), v_n(t) \in \mathbb{C}^N$, and $u_n(t+\Delta t) = \mathrm{e}^{-\mathrm{i}\hat{H}\Delta t}u_n(t)$, $v_n(t+\Delta t) = \mathrm{e}^{-\mathrm{i}\hat{H}\Delta t}v_n(t)$. Each of the N terms may be calculated independently; the calculation is thus trivially parallelizable in a manner that requires virtually no inter-thread communication. Note that in general this doubles the number of multiplications performed. This means that one has to run the simulation on more than two processors to see any reduction in the time required when compared to running serially.

Such a decomposition was proposed by Skinner and Glaser using the n-th eigenvector of $\hat{\rho}(0)$ as $u_n(0) = v_n(0)$, and the corresponding eigenvalue as w_n [3]. This method has several flaws in that computation of the eigenvectors is itself non-parallelizable and also that non-Hermitian density matrices cannot be decomposed in such a manner.

It is found that using a decomposition wherein the vector $u_n(0)$ is the n-th column of $\hat{\rho}(0)$, the k-th element of the vector $v_n(0) = \delta_{nk}$ where δ_{nk} is the Kronecker delta, and $\forall n, w_n = 1$ (a decomposition that avoids any calculations in the setup stage) leads to large increases in the speed of simulations and good scaling with the number of processors.

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Domain organization of YtvA studied by EPR

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The arrangement of the blue-light sensitive LOV and the STAS effector domain of the blue-light activated YtvA protein from B. subtilis was studied by EPR techniques using site-directed spin labeling with MTSL. MMM simulations were employed for data analysis [1].

Pulsed ELDOR on singly labeled protein showed a specific dimerization of YtvA in solution. ELDOR measurements of a mutant containing a flavin radical as well as data from doubly labeled mutants yield a dimerization scheme in which a LOV-LOV dimer is connected to a STAS-STAS dimer via a coiled-coil helix linker.

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Large Volume Aqueous Sample Holders at High Frequencies

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High field, high frequency EPR on aqueous samples has always been challenging due to the high dielectric losses of water, which have always severely restricted sample volume. This is also a major problem for DNP on aqueous samples where large volume samples are a prerequisite for major applications in NMR. This paper presents designs for non-resonant and resonant sample holders, which hold a relatively large volume of water, and use high power pulsed microwaves sources operating at kW power levels at W-band. Proof of principle experiments are conducted using both pulsed and CW techniques and design concepts for extensions to DNP are illustrated.

Investigations of Electronic Structure in Hetero-Dimers of Transition Ion Clusters

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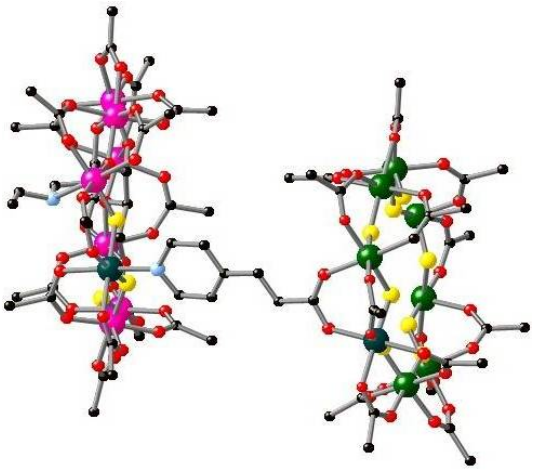

Structure of [Cr_7M]-{Cr_7M} hetero-dimers.

We have been investigating the chemistry and physics of transition metal clusters comprising anti-ferromagnetically coupled heterometallic rings ("Cr_7M"), which have a low but non-zero spin ground state. In this presentation I will discuss efforts to probe the electronic structure of supramolecular dimers of non-identical $Cr^{III}_7M^{II}$ clusters (M = Zn, Mn, Ni) as studied by multi-frequency Electron Paramagnetic Resonance (EPR) combined with approaches to modelling these very large spin systems.

The magnetic properties of the Cr_7Ni wheel have been well studied, showing the anti-ferromagnetic coupling of adjacent metal centres and an S = 1/2 ground state [1]. A family of related wheels have been formed with a different divalent metal, such as Cr_7Mn and Cr_7Zn. These compounds are isostructural with Cr_7Ni but with differing ground state spins.

The series of Cr_7M rings have been synthesized in both 'green' and 'purple' variations, named on account of their crystalline appearance. The green ring contains eight central μ_2-fluoride ions surrounding a templating ammonium cation. The purple variant is less geometrically symmetric and so exhibits greater magnetic anisotropy than the green counterpart.

By the simultaneous fitting of EPR and specific heat data, we have fits for the series of $Cr^{III}_7M^{II}$ single wheels where M^{II} = Ni, Mn and Zn. We are are currently in the process of simulating the full series of linked hetero-dimers to fit the exchange coupling between the rings.

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EPR study of triplet states in conductive polyaniline

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The magnetic properties of the conductive polymer polyaniline (PANI) and its derivatives have been studied extensively during the past decades. These properties are relevant for a better understanding of the nature of the charge carriers in the polymer structure. For example, most of the studied PANI derivatives showed a nearly linear temperature dependence of the magnetic susceptibility multiplied by temperature (χT *vs* T) which was attributed to disorder-induced localised polaron pairs (radical cation with S=1/2) [1]. A further study of the magnetic susceptibility suggests the coexistence of polarons and spinless bipolarons and the possible formation of bipolarons upon changing the temperature or doping level [2]. A slight deviation from the linear dependence of χT *vs* T usually was detected by SQUID at low temperature intervals, at T < 10K, for various PANI samples. In this low temperature region, the presence of magnetic field dependence of the magnetic moment was also noted. Recently, both of these magnetic properties were described by employing a "triplet'' model which used the distribution of the singlet-triplet splitting (E) with the density distribution function having a narrow peak near E=0 [3]. The present study was undertaken to look for the presence of such local triplet states in two types of PANI samples in order to more closely examine the nature of their distribution in these samples. It was expected that a characteristic EPR spectrum could be found and attributed to the excited triplet state with corresponding energy at low temperatures. The two types of PANI emeraldine salt samples investigated were the commercial "PANI K" (average M_w > 15,000, from Aldrich) and "PANI 1" produced enzymatically (with horseradish peroxidase) in aqueous solution by employing AOT vesicles as templates [4]. Evidence for the presence of thermally activated states was obtained by studying the temperature dependence of EPR spectral intensities and line widths in the low temperature region. The obtained activation energies for the thermally activated process are discussed in terms of expected energies for single-triplet transitions and possible exchange interactions. The obtained exchange interactions are correlated with different distributions of the polaron pairs in the PANI samples.

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Chemical Engineering of Molecular Qubits

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We show that the electron spin phase memory time, the most important property of a molecular nanomagnet from the perspective of quantum information processing, can be improved dramatically by chemically engineering the molecular structure to optimise the environment of the spin. We vary systematically each structural component of the class of antiferromagnetic Cr_7Ni rings to identify the sources of decoherence. The optimal structure exhibits a phase memory time exceeding 15 μs [1].

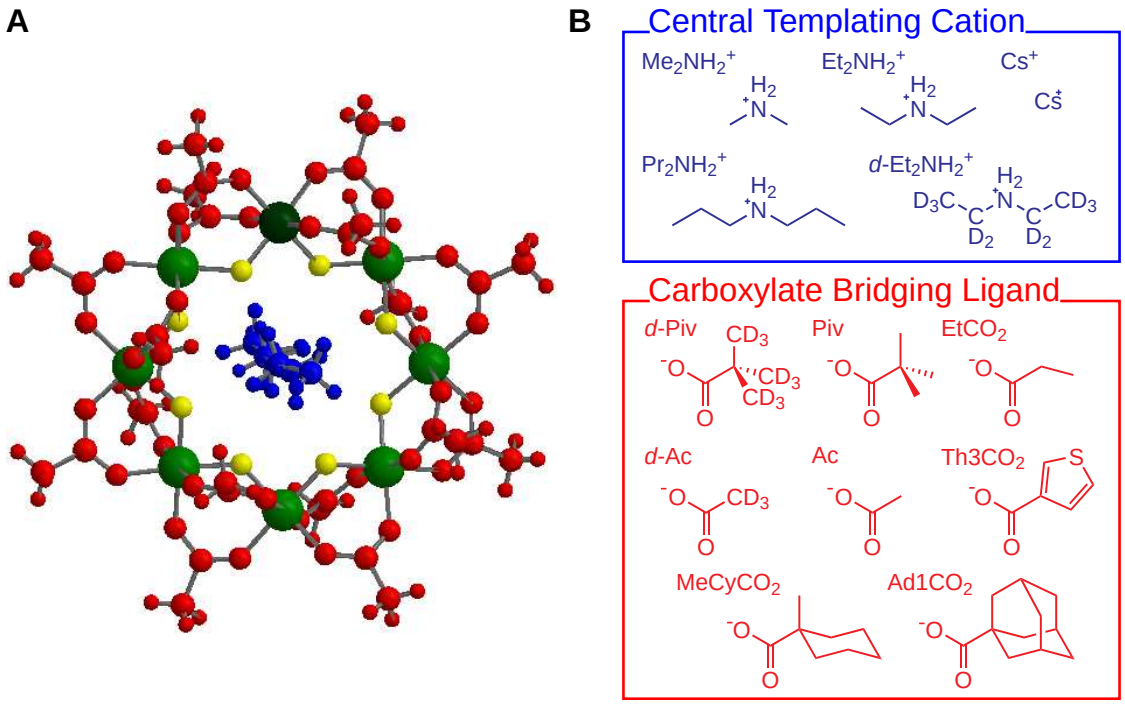

Figure 1: (A) Crystal structure of $[^{n}Pr_2NH_2][Cr_7NiF_8Ac_{16}]$ (B) Chemical structures of possible variants of the two key molecular building blocks.

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Tuning Molecular Magnets for Quantum Information Processing

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In the search for physical systems suitable for quantum computation, electron spins have naturally been proposed as candidates for elementary quantum bits (qubits). Crucially, materials exhibiting long electron spin coherence lifetimes with respect to the time taken for coherent manipulations are sought. To this end, molecular nanomagnets containing paramagnetic metal centres have emerged as intriguing systems of interest due to the controllable nature of the spin ground state. The Cr_7Ni family (S = 1/2 ground state), for example, has been identified as a potential single qubit system [1] with chemically 'tunable' properties. A recent study has demonstrated that chemical variation of the bridging ligand and central cation allows electron phase memory times of up to 15 μs to be observed at low temperatures. In particular, a comparison of electron phase memory times observed for protonated (^{1}H, I = 1/2) and deuterated (^{2}H, I = 1) Cr_7Ni molecules suggests that the extensive proton network, and corresponding large proton magnetic moment (γ_H), is one of the key challenges to obtaining long coherence lifetimes in these systems[2].

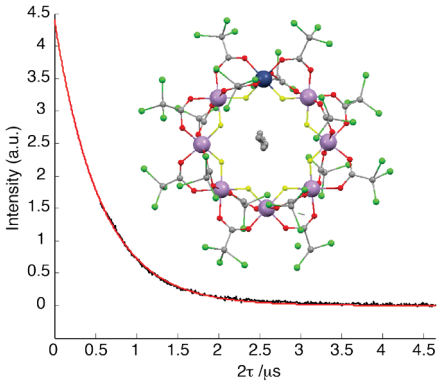

Figure 1. Electron spin-echo decay for a chlorinated (inset) Cr_7Ni molecular magnet in toluene at 5 K.

This work aims to further isolate the sources of electron spin decoherence in molecular magnets, initially by chemical substitution of the proton network with halogen elements [e.g. ^{35}Cl, ^{79}Br,^{81}Br (I = 3/2), and ^{19}F (I = 1/2)]. Coherence lifetimes (T_m) are presented for dilute, frozen solutions measured using 2-pulse Hahn-echo ESR experiments at X-band.

In addition, we explore avenues to use molecular nanomagnets as higher dimensional quantum-bit systems. The electron spin properties of asymmetric Cr_7Ni dimers are investigated as potential two-qubit systems capable of more complex quantum algorithms.

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Probing conformational changes upon GPCR activation by DEER

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G protein-coupled receptors (GPCRs) represent the largest class of membrane proteins encoded in the human genome [1]. They are of enormous pharmacological interest, with approximately 40% of drugs marketed as modulators of GPCR function [2,3]. However, structural information is scarce, with crystal structures obtained for only eight unique receptors to date [3, 4], which is largely due to the problems associated with successful overexpression, purification and crystallisation.

Neurotensin receptor 1 (NTS1) is one of few GPCRs that can be expressed in *E. coli* and purified in a functional, ligand-binding form for structural studies [5,6]. The neurotensin receptors have been postulated as potential targets for treatment of conditions such as schizophrenia and Parkinson's disease [7].

Our aim is to use site-directed spin labelling EPR spectroscopy to obtain structural information on NTS1. NTS1 is labelled with pairs of nitroxide spin labels on strategic positions to obtain information on NTS1 dynamics and to measure interhelix distances by DEER. Performing measurements on the receptor reconstituted into liposomes in the presence and absence of the agonist neurotensin [8] should give information on conformational changes occurring upon receptor activation. Ultimately, this study will advance our knowledge of how membrane-embedded GPCRs are activated for signalling through conformational changes, thus potentially aiding drug design.

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EPSRC National EPR Research Facility & Service

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The University of Manchester hosts the EPSRC National EPR Research Facility and Service, that accommodate several Bruker EPR instruments, allowing c.w. and pulsed EPR measurements at frequencies between 1 (L-band) and 95 GHz (W-band), a Quantum Design magnetometer and an ODESSA instrument (built by Nigel Poolton) that combines optically detected magnetic resonance (ODMR) with photo-EPR (both at 34 GHz). Together these make a unique research base for studying various types of paramagnetic species and materials. EPR is of wide application in chemistry, physics, materials, biology and medicine.

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

- Continuous wave (cw) EPR at 1, 4, 9, 24, 34 and 94 GHz frequencies (L-, S-, X-, K-, Q- and W-band).
- Pulsed EPR at 4, 9 and 34 GHz, for ESEEM, ENDOR, ELDOR and HYSCORE methods.
- Collaborative arrangements for pulsed EPR at 94 GHz, very high frequency cw EPR (100 – 750 GHz), and frequency domain EPR.
- "pump-probe" laser and electrochemical facilities.

Please contact us if you wish to discuss potential experiments, or go to:
http://www.epr.chemistry.manchester.ac.uk

Synthesis of Doubly Spin Labeled Myelin Basic Protein (MBP) and Structural Studies Using EPR Spectroscopy

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Myelin basic protein (MBP) maintains the tight multilamellar compaction of the myelin sheath in the central nervous system. The instability of myelin in multiple sclerosis (MS) is associated with the loss of positive charge in MBP as a result of posttranslational enzymatic deimination [1].

In this work, the conformation of individual, doubly labeled MBP molecules in large unilamellar vesicles mimicking the native myelin membranes (Cyt-LUVs) were illuminated to obtain insights into conformational changes upon deimination of MBP from the least modified, native ("healthy") rmC1 isoform to the highly modified and deiminated "MS" C8 form of MBP. The positions of the two labeling sites were varied to probe different amino acid positions in the protein. To this end, interspin distances of doubly-labeled MBP molecules are studied by CW EPR- and pulse EPR spectroscopy, based on the distance dependence of the dipole-dipole coupling between two spins.

Direct comparison between the data of the single and double mutants of MBP C1 and MBP C8 with respect to previously gained results, finally revealed structural differences for the "healthy" (C1) and "MS" (C8) state of the protein in its functional surroundings. From the combined EPR results it is found that MBP C1 charge mutants are more heterogeneous in their structure, which signifies its intrinsic disorder and flexibility, whereas the structure of the whole protein ensemble in C8 looks more widened. The conformation of the C8 variant in comparison to that of the C1 variant seems to lead to widened lateral (perpendicular to membrane plane) aggregation of myelin-like membranes, which lead to a diminished ability to cause adhesion of lipid bilayers. Moreover, in C1 charge mutants, the N- and C- termini are concealed within the lipid bilayer, whereas in C8, the N-terminus and the central helical region are more exposed, which may be correlated with the progression and/or the initiation of MS.

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Combining NMR docking data with EPR distances and *in silico* calculations for a more complete model of colicin protein-protein interactions

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Currently atomic resolution structures of protein-protein interactions are commonly limited to X-ray crystallography with its unnatural buffers, pHs and forced crystalline structure, while NMR developments have allowed for solution based structures of small complexes to be developed [1] however *ab initio* information still remains a developing field [2,3].

Site-directed spin labelling (SDSL) in combination with electron paramagnetic resonance (EPR) allows for the precise measurement of intra and intermolecular distances. Such distances traditionally are obtained using pulsed electron double resonance (PELDOR) techniques. New *in silico* methods now also allow for the comparison of computation and experimental data [4].

Using SDSL and distance measurements at several sites within a protein-protein complex allows for a three dimensional model to be built up using distance constraints, which when combined with NMR docking data and software gives a comprehensive model [5].

Using the well-characterised system, of colicin E9 and its cognate inhibitor, Im9 [6] a comprehensive solution is being developed to combine such NMR docking models, with PELDOR distance (and angle) constraints and *in silico* computations which are comparable to X-ray crystallographic models.

With this technique in place the model will be expanded to characterise other biologically relevant protein-protein interactions including the ill-defined non-cognate binding pairs of colicin E9 with the inhibitor proteins, Im2, Im7 and Im8.

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[6] Cascales et al, MMBR, 71, 1 (2007)

A “physiological” ST/EPR study: activation and superoxide radical production of NADPH-Oxidase in human monocytes

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In biological systems, reactive oxygen species (ROS) are generated by a variety of cellular sources, among which the NADPH oxidase enzymes (NOX) are a major class. They generate superoxide radicals $O_2^{-\bullet}$ by electron transfer from NADPH to molecular oxygen followed by H_2O_2 formation. Depending on location, concentration and type, ROS are involved in host defence by specialized immune cells, can serve as second messengers in many signalling cascades but also as toxins leading to induction of many pathological conditions. Hence, identification and quantification of ROS and oxygen consumption is of a high importance and a challenging task.

Here, we employ EPR spin trapping/monitoring to follow the evolution of the primary superoxide radical production by human $CD14^+$ monocytes which belong to the innate immune response system and express high amounts of NOX2. The NOX2 activation process is tightly regulated by cellular Ca^{2+} homeostasis.
In a first step the “physiological” conditions were optimized for EPR experiments and the redox properties of some cyclic hydroxylamines (CMH, CPH), which are redox activated spin monitors, and other traps were investigated. This included testing of different cell buffers for minimizing background radical production, controlling the effective cell numbers for various cell lines and donors and comparing sensitivity for different traps. The redox behaviour of a hydroxylamine trap was studied by cyclic voltammetry to understand its interaction with superoxide and redox active additives to define possible unwanted effects. Moreover, TAM-radicals were used simultaneously to follow oxygen consumption by activated cells.

For fresh human monocytes various stimuli, artificial and natural ones, were used to discriminate direct and Ca^{2+}-dependant pathways of NOX2 activation and to quantitatively measure the corresponding different superoxide production rates. Such data can be compared to more indirect biochemical or fluorescent methods assessing ROS formation. In addition, specific inhibitors of the activation pathways or of the NOX2 complex were examined. It was found that a Ca^{2+}-channel blocker is in fact also interacting with NOX2. We also demonstrate the strong antioxidant effect of ascorbic acid within the cellular system. The method can be used to characterize NOX(2) inhibitors important for clinical application but also to study effects of antioxidants on superoxide elimination.

Investigation of Free Radicals Formed in the Oxidation of Acoustically Levitated α-Pinene Droplets by EPR

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Free radicals control the lifetime of gases important for the Earth's radiative balance (e.g. CH_4), the budget of O_3 in all parts of the atmosphere, as well as the production of acidic species. Assessment of the variability of free radical formation from reactions of ozone with terpenes is important for understanding the health effects associated with the particulate matter[1]. Studies showed that a significant amount of reactive oxygen species is associated with secondary organic aerosol (SOA) formed under laboratory conditions during the reaction of α-pinene with ozone[2]. The α-pinene oxidation by ozone has been studied in individually levitated aerosol droplets using an acoustic levitator at 100 kHz encased in a custom-built environmental chamber allowing control of the gas-phase surroundings and relative humidity.[3]

Figure 1: Images of a α-pinene droplet levitated in an ultrasonic trap.

In order to determine the chemical composition of free radical species a spin trap was employed to stabilize the radicals and increase their lifetimes for characterisation[4].

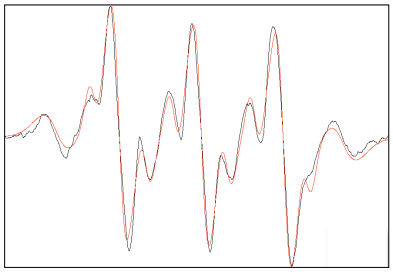

Figure 2: Experimental EPR spectrum (in black) together with a computer simulated spectrum (in red) from the oxidation of levitated α-pinene droplets with ozone by EPR using a DMPO spin trap. The fitting was achieved with the following simulation parameters based on a mixture of three species: one oxygen-centred radical (5% of the total), with hyperfine couplings a_N=13.54 G and a_H=8.73 G, one carbon centred radical (~20%) with a_N=14.37 G and a_H=19.41 G and a decomposition spin-adduct (~75%) with a_N=13.85 G. The EPR spectra were recorded at ambient temperature on a JEOL FR30EX spectrometer. Our study demonstrates that it is possible to analyse free radicals by EPR formed from the oxidation of α-pinene in a containerless environment with applications to studies of reaction mechanisms in atmospheric science and beyond.

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Exploring Pluronic F127/cyclodextrin systems using EPR and fluorescence probe methods

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Pluronic PEO-PPO-PEO triblock copolymers have the property to form micelles or gel phases in aqueous solutions as a function of concentration and temperature [1].

The behaviour of some solutions of Pluronic F127 (16. 6 %) function of temperature and concentration of hydroxy propyl-β-CD (HPB) was investigated by fluorescence and EPR probe methods. Pluronic block copolymers have the property to form inclusion complexes with cyclodextrins and this can influence the phase transformation from micelles to gel of the polymer. EPR and fluorescence spectra often reflect the polarity properties of the microenvironment around the probe and provide information on their dynamic [2,3]. The spin and fluorescence probes used in this study are presented in figure 1.

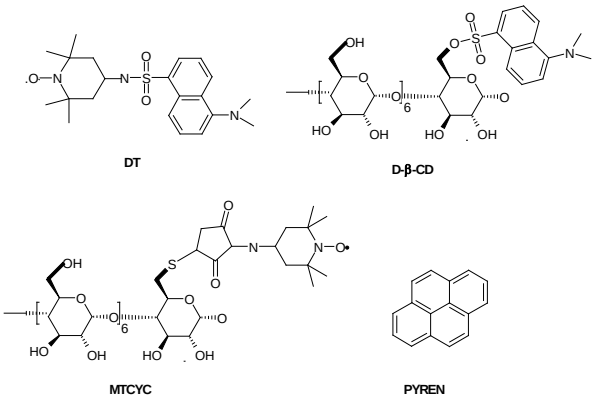

Figure 1. Fluorescence and spin probes.

We found that the spin probe or fluorescence probes with an enhanced affinity for the polymeric chain (like spin labelled or fluorescence labelled cyclodextrins) can report better on the phase transformations occurring in the Pluronic F127 solutions as a function of temperature and concentration of HPB.

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Electron delocalization in multi-porphyrin systems probed by EPR

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Linear and cyclic π-conjugated multi-porphyrin systems are currently being studied for potential applications as NIR-emitters [1], molecular wires [2] and dye-sensitized solar cells. The understanding of the energy distribution and charge circulation in these systems is paramount for any further development of these technologies.

The electron distributions in radical cations of linear butadiyne-linked Zn porphyrin oligomers (Figure 1) and a cyclic six-membered nanoring [3] are investigated by continuous wave and pulse EPR techniques. Room temperature and frozen solution measurements are performed at X- and W-band and compared for the series of oligomers from monomer to hexamer and with the six-membered nanoring. Increasing delocalization of electron density results in the electron spin experiencing an averaged hyperfine influence from a number of porphyrin units, which in turn leads to narrowing of the EPR line width [4,5] as easily measured at X-band. Measurements performed over a wide temperature range will provide further insight into the nature of the electron delocalization.

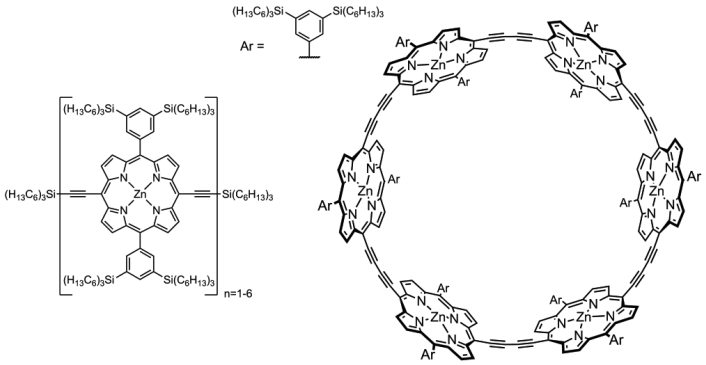

Figure 1. Structures of the oligomers and the nanoring

The change of proton and nitrogen hyperfine interactions along the series of oligomers is monitored by ENDOR and HYSCORE measurements in frozen solution. DFT geometry optimizations and calculations of the magnetic hyperfine interactions will aid the interpretation of the experimental data. The results provide an overall picture of the distribution of the electron wavefunction over the different porphyrin units in the linear oligomers and in the ring.

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An EPR & ENDOR study of the counter ion effects in Cu-bis(oxazoline) asymmetric catalysts.

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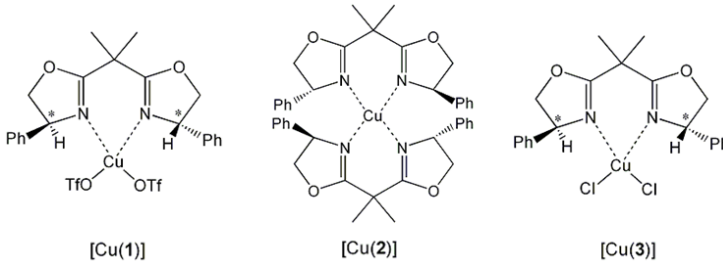
Enantioselective, asymmetric synthesis involves the preparation of chiral compounds with defined three-dimensional stereochemistry. Enantiomerically pure compounds are vital for many applications, for example, in the pharmaceutical industry, for vitamins and flavourings and in nonlinear optical and liquid crystalline materials. A wide range of synthetic catalysts are now available (BINOLs, cinchona alkaloid derivatives, TADDOL complexes) that attain excellent levels of ee's in reactions such as aldol condensations, Diels-Alder, cyclopropanations and aziridinations. One such series of Cu(II) based complexes are based on the chiral Bis-oxazoline ligands (BOX) including the homoleptic and heteroleptic complexes shown below:



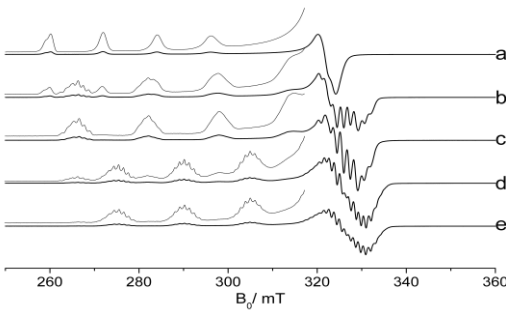


Fig.1: X-band CW-EPR spectra (140 K) of [Cu(OTf)2] after addition of increasing BOC ligand ratios; (a) 1: 0 (b) 1:1 (c) 1:2 and (d) 1:6.

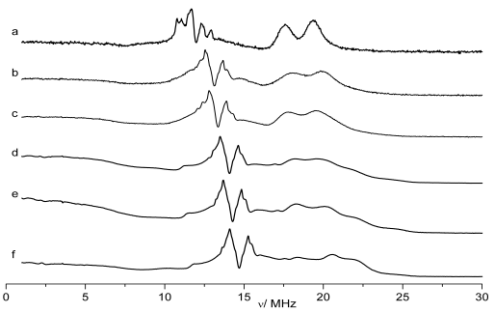


Fig.2: Angular selective X-band Davies ENDOR spectra (10K) of [Cu(**1**)].

Since the complexes are prepared in situ, little is known about the nature of the actve catalyst during the reaction. Furthermore, it is know that the counterion (Cl vs OTf) plays an important role in the catalytic activity, but the origin of this is unknown. We are therefore prepared a series of Cu-BOX complexes (1-3) and studied their electronic properties and ligand structure using EPR and ENDOR spectroscopy. Significant differences in the *g/A* parameters are observed in [Cu(**1**)] compared to [Cu(**3**)], whilst the ENDOR spectra of the three complexes are also substantially different. Here we report on the spectroscopic properties of these complexes and their changes in structure for the Diels Alder reaction.

Spin Delocalisation in Transition Metal Tris(dithiolene) Complexes

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The first ever coordination compound to break the cardinal rule that six-coordinate equals octahedral, was the trigonal prismatic neutral rhenium tris(dithiolene).[1] Since that poignant moment, several other tris(dithiolene) compounds have crystallized with trigonal prismatic geometry, thus inspiring spectroscopic and theoretical studies directed at explaining this unusual phenomenon. However, still to this day, the true electronic structure of this class of compounds remains ambiguous. We have employed the simplest dithiolene ligand, edt = ethene-1,2-dithiolate, where the proton substituents attached to the olefinic carbons are neatly poised to report on the extent of spin (de)localization in such moieties. We have examined $[V(edt)_3]^0$, $[V(edt)_3]^{2-}$, and $[Mo(edt)_3]^{1-}$ (all $S = {}^1/_2$) by EPR and ENDOR spectroscopies, including TRIPLE. The cw spectra indicate the two vanadium compounds as metal-centered paramagnets, while the molybdenum compound is ligand-centered. Despite this distinction, the magnitude of the proton coupling to the unpaired spin is approximately the same for all three species, and is a consequence of their trigonal geometry.

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Probing the Coupling between Molecular Spin Qubits by EPR Spectroscopy

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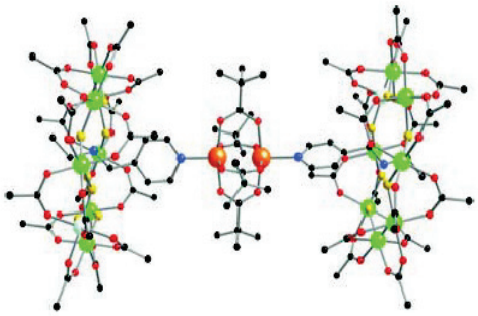
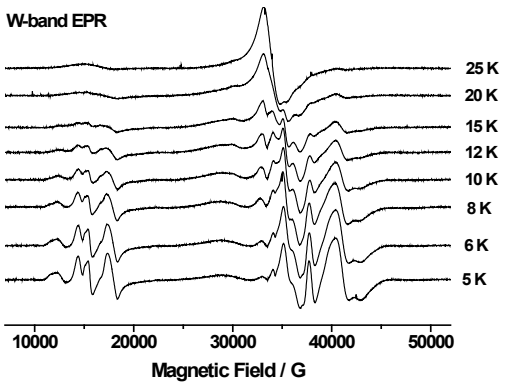
It has been proposed[1,2] that heterometallic molecular clusters with antiferromagnetic (AF) internal coupling are suitable electronic spin systems for qubit encoding and implementation of quantum logic gates. Supramolecular chemistry gives the possibility to engineer such molecules and assemble them into dimers or polymers via electronic linkers.[3] This allows control over magnetic interactions.

We present here our recent results on EPR characterization of new magnetic molecules that show potential for quantum computing. Such an example is the molecule presented below, where two AF $\{Cr_7Ni\}$ rings with S = ½ ground states are coupled to each other via the paramagnetic $\{Ru_2(Me_3CCO_2)_4\}^+$ unit. Variable temperature multi-frequency (9-95 GHz) EPR spectroscopy has been applied to determine details of the electronic structure, as well as spin dynamics in these and related compounds.





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A Dual Sensor Spin Trap for Use with EPR Spectroscopy

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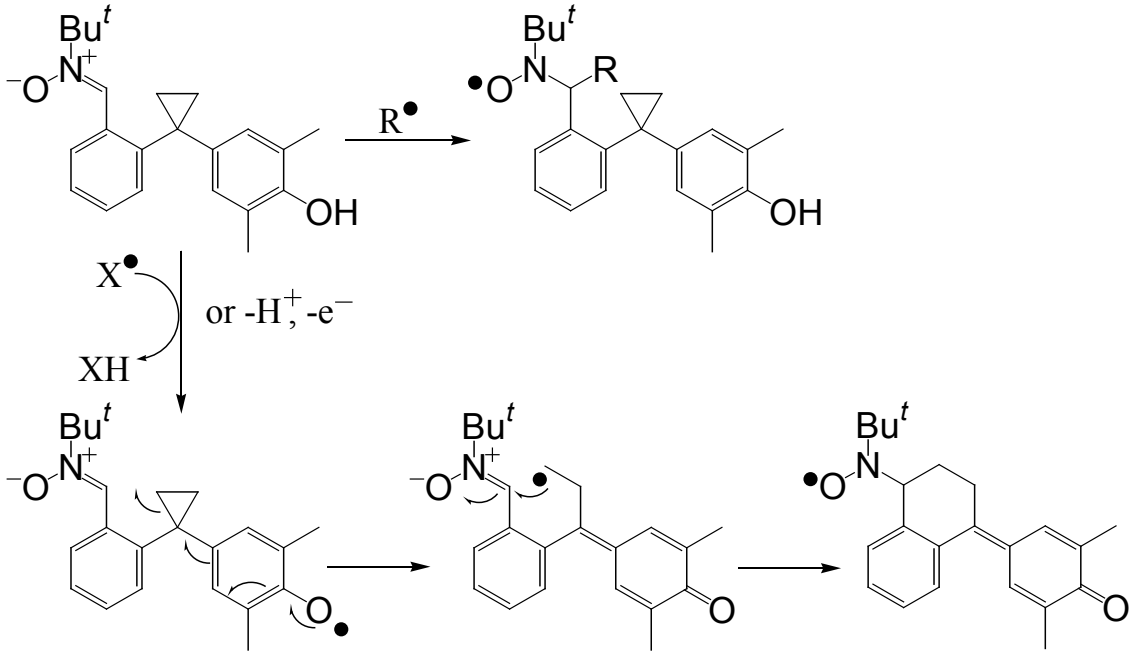
Redox active metal ions, carbon-centred radicals, and oxygen-centred radicals are all important in oxidative stress. A radical detector combining a nitrone spin trap, a phenol, and two non-communicating aromatic rings linked by a cyclopropane, which acts as a radical clock-like unit, has been prepared to detect and to distinguish between these different types of oxidants.

Electron rich radicals should form adducts with the nitrone, while electron poor species are expected to react with the phenol *via* hydrogen abstraction followed by cyclopropane ring-opening giving an unstable radical, which will then cyclize onto the nitrone.



X-band EPR spectroscopy has shown that iron(III) reacts with the phenol unit inducing opening of the cyclopropane ring and cyclization to generate a stable nitroxyl radical, while hydroxyl and methyl radicals both react directly with the nitrone to yield stable nitroxide radical adducts.[1]

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An EPR study of the radical ions of cycloheptatrienyl molybdenum complexes

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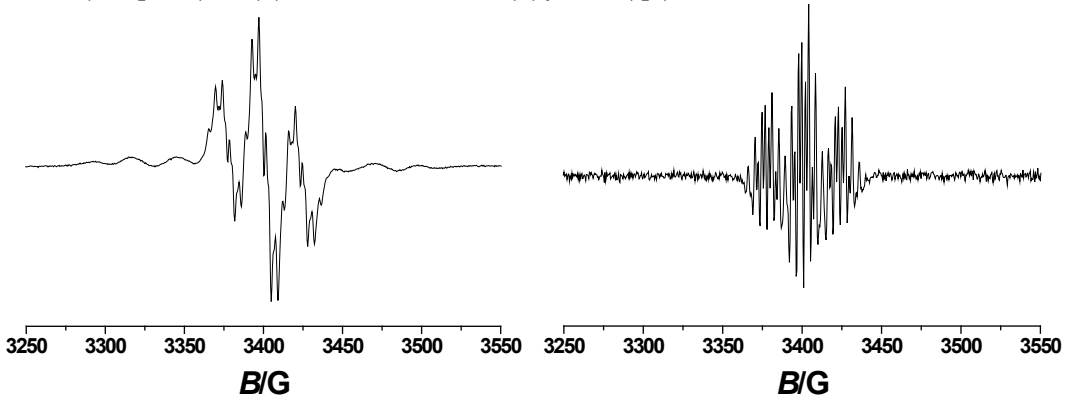
Cycloheptatrienyl molybdenum complexes can easily undergo reversible one-electron oxidation to their corresponding radical cations, which are relatively stable and some of the complexes also undergo reversible two-electron oxidation. These compounds are of interest as 'molecular wires' for their potential use in the development of molecular electronics.

We have studied fluid solution X-band EPR spectroscopy of a range of these complexes in dichloromethane, with the radical cations generated either electrochemically or using a chemical oxidant (e.g. $[Fe(\eta\text{-}C_5H_5)_2]^+$). A series of complexes of the type $[MoX(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]^{z+}$ with a variety of ligands X has been prepared to investigate the effect of X on the electronic structure. In addition, for one complex the dppe ($Ph_2PCH_2CH_2PPh_2$) has been substituted by bipy or Bu^t-bipy and some complexes of the type $[\{Mo(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)\}_2(\mu\text{-}X)]^{z+}$ have also been studied.

Optimal resolution of the fluid solution EPR spectra was achieved for all the complexes at *ca.* 243 K and all showed well-resolved spectra for molybdenum isotopes split by the ligand hyperfine interactions. The molybdenum hyperfine splittings could be easily obtained from the first derivative spectra. However, second derivative spectra were recorded in order better to observe and then to simulate the hyperfine splittings to the ligands. Example first and second derivative spectra for one of the complexes are shown below (for $[Mo(C_4H)(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]^+$).



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