



EFEP R 2019

XI<sup>th</sup> EFEP R 2019

Conference

September 1-5

Bratislava, Slovakia



STU

SLOVAK UNIVERSITY OF  
TECHNOLOGY IN BRATISLAVA





**XI<sup>th</sup> EFEPR Conference,  
1-5 September 2019,  
Bratislava (Slovakia)**

**Book of Abstracts**

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## **Welcome to EFEPR 2019**

The local organizing committee, Slovak Chemical Society and the Slovak University of Technology in Bratislava welcome you at the **XI<sup>th</sup> Conference of the European Federation of EPR groups**.

The **EFEPR** is a non-formal organization gathering 14 national EPR groups from European and extra-European Countries and the EFEPR conference series is one of the prime international forums to present the progress in EPR spectroscopy, including new experimental and theoretical methodologies. During the successful X<sup>th</sup> EFEPR Conference in Torino (Italy) in September 2016, the capital of Slovakia was suggested as the next location and it is our great pleasure to host you all in **Bratislava** during **September 1-5, 2019**. We thank you for supporting the EFEPR Conference series.

Special thanks go to the members of the International Advisory Board for their assistance with the selection of invited speakers, evaluation of abstracts and for their active promotion of XI<sup>th</sup> EFEPR Conference throughout the global EPR community.

The scientific sessions of XI<sup>th</sup> EFEPR Conference are headlined by 7 plenary and 7 keynote speakers and the conference program includes the activities of the International EPR (ESR) Society (IES) and EFEPR with the specially allocated sessions. IES and the Slovak Chemical Society sponsor the student awards for the best posters presented at the Conference.

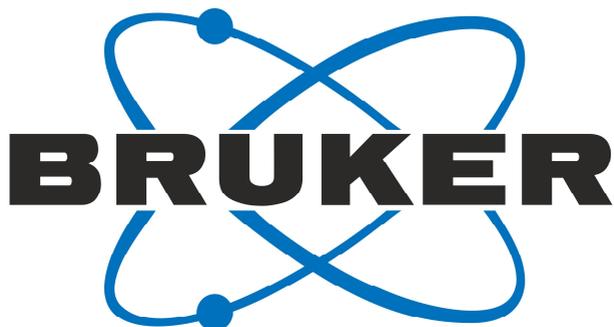
We also thank the organizing institution, the Slovak University of Technology in Bratislava, along with the International EPR (ESR) Society, Slovak Chemical Society and all partners and sponsors for the support of Conference.

We wish all participants a pleasant stay in Bratislava and Slovakia and hope you will enjoy the scientific as well as the social program of the XI<sup>th</sup> EFEPR Conference. The enthusiastic discussions, constructive arguments and suggestions and the establishment of friendship ties between delegates from all corners of Europe will represent the real proof of its success.

Bratislava, August 2019

*Peter Rapta and the Local Organizing Committee*

## Partners and Sponsors



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Prof. **Vlasta Brezová**  
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Dr. **Karol Lušpai**  
Dr. **Peter Poliak**  
Prof. **Peter Rapta**  
Prof. **Marián Valko**  
Dr. **Michal Zalibera**

## General information for participants

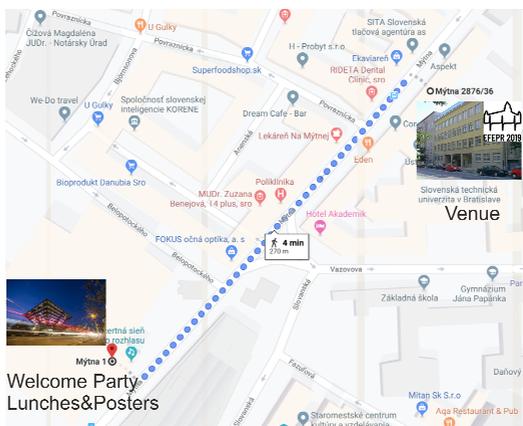
### 1.1 Registration and Welcome party

Registration and the welcome Party will be organized on Sunday 1<sup>st</sup> September 2019 from 18:30 to 20:30 in the foyer of the „inverted pyramid“ building of the Slovak Radio at Mýtna 1 (see map).



### 1.2 Conference Venue

The conference will take place in the Auditorium of Dionýz Ilkovič of the Slovak University of Technology in Bratislava, at Mýtna 36. The hall is located in the city centre (see map).



### 1.3 Conference Office

The registration desk will be open on Sunday 1<sup>st</sup> September 2019 from 18:30 to 20:30 in the foyer of the Slovak Radio Building (inverted pyramid) at Mýtna 1. From Monday 2<sup>nd</sup> September 2019 it will be located in front of the entrance to the main lecture hall at Mýtna 36, opening from 8:00 and available during coffee breaks and lunches.

## **1.4 Public transportation**

The public transportation system consists of buses, trolley-buses and trams and is a good choice if you need to get out of the city centre, which otherwise is well accessible on foot. The vehicles operate from early morning (around 4:00) and end around midnight. The tickets must be purchased prior to entering a vehicle – at the ticket machines available at most of the stops, newspapers kiosks or special public transportation shops. The shortest 15 min tickets cost 0.70 € but a more useful 60 min fare is available for 1.20 €. You can also purchase a ticket by sending a blank text message (40 min/1 € SMS to number 1140, 70 min/1.30 € SMS to 1100 or 24 h/4.50 € SMS to 1124) or by using a mobile app. After getting on the vehicle, you need to mark the ticket in a special machine which is built in each bus, trolley-bus and tram – otherwise, if you are caught, you can get a fine of 50 €. The same goes for the text message ticket – you need to have a return SMS prior to entering the vehicle. More info <https://imhd.sk/ba/public-transport>,

As an alternative to public transportation, a bike-sharing system is available in the city and more info can be found at <https://slovnaftbajk.sk/en>.

## **1.5 Internet-WiFi**

The **eduroam** free wireless (WiFi) service is available at the conference site. WiFi connection will also be available for people without access to eduroam and the login credentials will be provided at registration.

## **1.6 Speakers**

Speakers are asked to bring their presentation to the conference room at least 15 min before the session starts. Members of the local organizing committee will be available to assist in uploading the presentations.

## **1.7 Posters**

Posters will be exposed during the first half of the conference Sun 1<sup>st</sup> - Tue 3<sup>rd</sup> September in the Slovak Radio Building, where lunches and Poster sessions will take place. The poster holders will be numbered in the same way as the poster abstract in the abstract book. The first poster session on Monday 2<sup>nd</sup> is dedicated to odd-numbered posters and the second on Tuesday 3<sup>rd</sup> to the even ones. Presenters are kindly asked to remove their posters after the second poster session since the hall will no longer be available for the conference.

Two poster prizes will be awarded by the International Electron Paramagnetic Resonance Society (IES) and a third prize donated by the Slovak Chemical Society. Poster awards will be hand out on Wednesday 4<sup>th</sup> during the IES dedicated session.

## **1.8 Coffee breaks and meals**

Coffee breaks will be served in the foyer in front of the conference hall. Lunch meals will be served in the Slovak Radio Building on Monday and Tuesday and in front of the conference hall on Wednesday and Thursday.

## **1.9 Social events**

A Welcome Reception will be held on Sunday 1<sup>st</sup> September from 18:30 to 20:30. There will be a drink reception and buffet on Monday accompanying the poster session after the Bruker presentation from 18:00 sponsored by Bruker.

Wednesday afternoon will be dedicated to social activities. For registered participants, three tours have been prepared.

### **Bratislava City Tour**

The Prešporáčik® Oldtimer sightseeing vehicle will drive you around the most interesting streets and highlights of Bratislava. Afterwards, you will discover the charming Old Town with elegant palaces and quaint squares revealing the legends and life in the royal town with a professional guide during a walking tour at the pedestrian zone of the historical centre.

**Pick up point:** Historical building of Slovak National Theatre, Hviezdoslavovo sq. 1

**Time:** 15:00

**Expected duration:** 2 hours

### **Devín Castle Tour**

The impressive ruins of the Devin Castle are set in the beautiful natural scenery towering over the confluence of two rivers Danube and Morava, forming the border with Austria. In the cosy local wine tavern "Viecha Sv. Urbana v Devíne", situated just a few minutes walk from the castle, you will experience the traditional taste of currant wine, typical for this region.

**Pick up point:** FCHPT Radlinského 9

**Time:** 15:00

**Expected duration:** 3 hours

### **Wine Tasting Tour**

Authentic Slovakian wine tasting in Small Carpathian Wine Region, which is Slovak biggest wine district, will take place in Karpatská Perla (Carpathian Pearl) a Slovak family-owned winery located in the village of Šenkvice. The owners try to preserve the traditions and heritage of their ancestors and produce the wines, which reflect the terroir of the vineyards and unique varietal characteristics.

**Pick up point:** FCHPT Radlinského 9

**Time:** 15:00

**Expected duration:** 3 hours

## 1.10 Gala dinner

The conference gala dinner will take place at the Castle Restaurant „Hrad“ located directly below Bratislava Castle offering a magnificent view of old Bratislava. As the restaurant is within walking distance from the conference venue (30 min) and all of the suggested hotels you can take a nice walk through the historical city centre to get there. It can be reached by the public transport trolley bus line 203 or 207 bus stop Zámocká (see the map below).



## 1.11 Local organizer contacts

|                     |                     |
|---------------------|---------------------|
| Michal Zalibera     | cell: +421907297952 |
| Peter Rapta         | cell: +421907030013 |
| Zuzana Barbieriková | cell: +421908210187 |

## Tourist information

### PUBLIC TRANSPORT

<https://imhd.sk/ba/public-transport>

### RESTAURANTS

Authentic Slovak restaurants

|  |                    |  |    |
|--|--------------------|--|----|
| <b>Slovak Pub</b>                      |                    |  | €€ |
| Obchodná 2                             | ☎ +421 252 926 367 | <a href="http://www.slovakpub.sk">www.slovakpub.sk</a>                             |    |
| <b>Bratislava Flag Ship Restaurant</b> |                    |  | €€ |
| Námestie SNP 8                         | ☎ +421 917 927 673 | <a href="http://www.bratislavskarestauracia.sk">www.bratislavskarestauracia.sk</a> |    |

Other restaurants

|   |                      |   |        |
|---|----------------------|---|--------|
| <b>Bratislavský Meštiansky Pivovar</b>    |                      |   | €€/€€€ |
| Drevená 8                                 | ☎ +421 944 512 265   | <a href="http://www.mestianskypivovar.sk/home">www.mestianskypivovar.sk/home</a>        |        |
| Dunajská 21                               | ☎ +421 948 710 888   | <a href="http://dunajska.mestianskypivovar.sk">http://dunajska.mestianskypivovar.sk</a> |        |
| <b>Savage Garden Bar &amp; Restaurant</b> |                      |   | €€/€€€ |
| Námestie slobody                          | ☎ +421 917 115 116   | <a href="http://www.savagegarden.sk">www.savagegarden.sk</a>                            |        |
| <b>ROXOR</b>                              |                      |   | €/€€   |
| Šancová 19                                | ☎ +421 2/210 205 00  | <a href="http://roxorburger.sk">http://roxorburger.sk</a>                               |        |
| <b>Minerva</b>                            |                      |   | €/€€   |
| Michalská 3                               | ☎ +421 (2)544 312 14 | <a href="http://bissburger.sk">http://bissburger.sk</a>                                 |        |
| <b>Pivovar Alžbetka</b>                   |                      |   | €/€€   |
| Mickiewiczova 1                           | ☎ +421 905 534 102   | <a href="http://www.pivovaralzbetka.sk">www.pivovaralzbetka.sk</a>                      |        |
| <b>Bistro St. Germain</b>                 |                      |   | €€/€€€ |
| Rajská 7                                  | ☎ +421 911 331 999   |   |        |
| <b>Gatto Matto Ristorante</b>             |                      |   | €€/€€€ |
| Panska 17                                 | ☎ +421 (2)544 384 08 | <a href="http://www.gattomatto.sk/ristorante">www.gattomatto.sk/ristorante</a>          |        |
| <b>Jasmin</b>                             |                      |   | €€/€€€ |
| Židovská 7                                | ☎ +421 (2)544 151 82 | <a href="https://www.jasmin1.sk">https://www.jasmin1.sk</a>                             |        |

### PUBS

|                     |                       |
|---------------------|-----------------------|
| <b>Meetnica</b>     | Mýtna 19              |
| <b>Urban pub</b>    | Mýtna 35              |
| <b>La Putika</b>    | Mýtna 39              |
| <b>Kollarko</b>     | Kollárovo námestie 23 |
| <b>Bukowski Bar</b> | Námestie SNP 24       |

## Conference Program

### Sunday 1.9.

|             |                                       |   |
|-------------|---------------------------------------|---|
| 18:30-20:30 | <i>Registration and Welcome Party</i> | Foyer<br>Slovak Radio Building, Mýtna 1 |
|-------------|---------------------------------------|---|

### Monday 2.9.

|                  |                         |   |
|------------------|-------------------------|---|
| 08:45-09:00      | <i>Opening</i>          |   |
| <b>Session 1</b> |                         | <b>chair: Aharon Blank</b>  |
| 09:00-09:45      | PL1 Roberta Sessoli     | Magnetic molecules for the second quantum revolution: from hybrid nanostructures to electric field control  |
| 09:45-10:15      | KN1 Jens Anders         | EPR-on-a-chip: A new paradigm in EPR spectroscopy   |
| 10:15-10:35      | OP1 Alexander Schnegg   | Magneto-Structural Correlations in Six- to Two-Coordinate Cobalt Complexes with Large Magnetic Anisotropies   |
| 10:35-11:05      | <i>Coffee Break</i>     |   |
| <b>Session 2</b> |                         | <b>chair: Alex Smirnov</b>  |
| 11:05-11:35      | KN2 Matvey Fedin        | EPR of metal-organic frameworks: from defects elucidation to new functionalities  |
| 11:35-11:55      | OP2 Thilo Hetzke        | Binding of tetracycline to its aptamer determined by 2D correlated Mn <sup>2+</sup> hyperfine spectroscopy  |
| 11:55-12:15      | OP3 Ivan Sudakov        | Combined EPR and ODMR approach to study degradation of fullerene-free organic solar cell materials  |
| 12:15-12:35      | OP4 Angeliki Giannoulis | EPR probes two closed ATP/ADP conformations and small nucleotide-driven structural changes in yeast Hsp90 chaperone   |
| 12:35-14:30      | <i>Lunch</i>            |   |
| <b>Session 3</b> |                         | <b>chair: Etienne Goovaerts</b>   |
| 14:30-15:00      | KN3 Helene Bolvin       | First principles determination of EPR parameters in a triple decker of cerocene   |
| 15:00-15:20      | OP5 Floriana Tuna       | EPR Spectroscopy of f-Block Organometallic Compounds  |
| 15:20-15:40      | OP6 George Mitrikas     | Strain Effects of <sup>31</sup> P Hyperfine Coupling Constants in the Conformationally Flexible [Cu{Ph <sub>2</sub> P(O)NP(O)Ph <sub>2</sub> } <sub>2</sub> ] Complex, as Revealed by HYSORE Spectroscopy |

|                  |  |  |
|------------------|--|--|
| 15:40-16:00      | OP7 Max Schmallegger                       | The Bifunctional Chemistry of Bis(acyl)phosphane Oxides in Aqueous and Alcoholic Media |
| 16:00-16:30      | <i>Coffee Break</i>                        |  |
| <b>Session 4</b> |  | <b>chair: Stephen Sproules</b>   |
| 16:30-17:15      | PL2 Christiane Timmel                      | Putting a New Spin on Porphyrin Molecular Wires  |
| 17:15-18:00      | BR1 Bruker Presentation                    | Bruker's latest EPR developments   |
| 18:00-20:00      | <i>Poster Session and Bruker Reception</i> |  |

**Tuesday 3.9.**

|                  |                          |   |
|------------------|--------------------------|---|
| <b>Session 5</b> |                          | <b>chair: Inés García Rubio</b>   |
| 09:00-09:45      | PL3 Olav Schiemann       | Pulsed Dipolar Spectroscopy: From Model Systems to Cells  |
| 09:45-10:15      | KN4 Marilena Di Valentin | Light-induced pulsed EPR dipolar spectroscopy: the triplet state probe                                      |
| 10:15-10:35      | OP8 Pia Widder           | Nitroxide spin labeling with copper click chemistry   |
| 10:35-11:05      | <i>Coffee Break</i>      |   |
| <b>Session 6</b> |                          | <b>chair: Thomas Prisner</b>  |
| 11:05-11:35      | KN5 Maxie Roessler       | Protein film electrochemical EPR spectroscopy as a technique to investigate redox reactions in biomolecules |
| 11:35-11:55      | OP9 Tatyana Smirnova     | Electrostatics in Solid-Supported Lipid-Protein Systems   |
| 11:55-12:15      | OP10 Timothee Chauvire   | Microtubule (MT) Binding Domain of tau protein studied by cw-ESR and pulsed ESR analysis                    |
| 12:15-12:35      | OP11 Hiroshi Hirata      | In vivo extracellular pH mapping of tumor mouse models using EPR  |
| 12:35-14:30      | <i>Lunch</i>             |   |
| <b>Session 7</b> |                          | <b>chair: Sabine Van Doorslaer</b>  |
| 14:30-15:15      | PL4 Herve Vezin          | EPR and Industry applications   |
| 15:15-15:35      | OP12 Andrea Folli        | A unique dual-mode microwave EPR reactor-resonator for T-jump experiments                                   |
| 15:35-15:55      | OP13 Thorsten Bahrenberg | Methodological advances of W-band DEER with shaped pulses   |
| 15:55-16:30      | <i>Coffee Break</i>      |   |
| <b>Session 7</b> |                          | <b>chair: Peter Rapta</b>   |
| 16:30-16:50      | OP14 Alice Bowen         | OPERA: Out of Phase Experiment RIDME Application.   |

|             |                       |   |
|-------------|-----------------------|---|
| 16:50-17:10 | OP15 Daniel Klose     | Excitation and readout of methyl group tunnel state coherence by pulse EPR spectroscopy |
| 17:10-18:00 | <i>EFEP Assembly</i>  |   |
| 18:00-20:00 | <i>Poster Session</i> |   |

**Wednesday 4.9.**

|                  |                             |  |
|------------------|-----------------------------|--|
| <b>Session 8</b> |                             | <b>chair: Wolfgang Lubitz</b>  |
| 09:00-09:45      | PL5 David Britt             | EPR Spectroscopy of [FeFe] Hydrogenase H-Cluster Bioassembly Intermediates   |
| 09:45-10:15      | KN6 Benesh Joseph           | Membrane transport explored with pulsed ESR spectroscopy   |
| 10:15-10:35      | OP16 Edward Reijerse        | The electronic structure of the H-cluster in [FeFe] hydrogenase as analyzed through Q-band <sup>13</sup> C ENDOR spectroscopy. Implications for the catalytic mechanism. |
| 10:35-11:05      | <i>Coffee Break</i>         |  |
| <b>Session 9</b> |                             | <b>chair: Hitoshi Ohta</b>   |
| 11:05-11:25      | OP17 Petr Neugebauer        | Contactless millimeter wave method for quality assessment of large area graphene   |
| 11:25-11:45      | OP18 Athanassios Boudalis   | Magnetolectric coupling in spin triangles  |
| 11:45-12:05      | OP19 Anastasiia Kul'taeva   | Powder and single crystal CW and Pulse EPR Studies of Alkene Adsorption over Cu <sub>2.931</sub> Zn <sub>0.069</sub> (btc) <sub>2</sub>                                  |
| 12:05-13:00      | <i>IES Assembly</i>         |  |
| 13:00-14:00      | <i>Lunch</i>                |  |
| 14:00-19:00      | <i>Free Afternoon/Trips</i> |  |
| 19:00-22:00      | <i>Gala Dinner</i>          |  |

**Thursday 5.9.**

|                   |                     |  |
|-------------------|---------------------|--|
| <b>Session 10</b> |                     | <b>chair: Lukáš Bučinsky</b>   |
| 09:00-09:45       | PL6 Vladimir Malkin | Calculations and interpretation of the EPR parameters in the framework of 2- and 4-component DFT approach                                  |
| 09:45-10:15       | KN7 Alexey Popov    | Endohedral spins in carbon cages   |
| 10:15-10:35       | OP20 Antonio Barbon | Precise determination of the direction of the transition dipole moment by the study of the magnetophotoselection effects in triplet states |
| 10:35-11:05       | <i>Coffee Break</i> |  |

| <b>Session 11</b> |                          | <b>chair: Elio Giamello</b>  |
|-------------------|--------------------------|--|
| 11:05-11:25       | OP21 Jabor Rabeah        | Simultaneously Coupled 4 in 1 Operando EPR/XAS/ATR-IR/UV-vis Spectroscopy for Monitoring Catalysts at Work |
| 11:25-12:10       | PL7 Mario Chiesa         | Surface Chemistry and Catalysis by EPR: Concepts, Examples and Perspectives.                               |
| 12:10-12:30       | OP22 Bela Bode           | EPR spectroscopy provides insights into Cr/PNP based ethylene tetramerisation catalysis                    |
| 12:30-12:50       | OP23 Zuzana Barbieriková | Identification of reactive radical intermediates in photocatalytic systems by indirect EPR techniques      |
| 12:50-13:00       | <i>Closing</i>           |  |
| 13:00-14:00       | <i>Lunch</i>             |  |

## **Oral Contributions**

### **Abstracts**

- **Plenary Lectures** PL
- **Kenotes** KN
- **Oral Presentations** OP



## **Plenary Lectures**



## Magnetic molecules for the second quantum revolution: from hybrid nanostructures to electric field control

Roberta Sessoli<sup>1</sup>

1) *Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, Italy*

Implementation of modern Quantum Technologies might benefit from the remarkable quantum properties shown by molecular spin systems. In the field of quantum information technology several physical realizations of the basic unit, or qubit, are currently investigated. Actually, the most advanced platform is constituted by superconducting circuits, but spin systems continue to attract interest as intrinsic two-level systems, which can be easily manipulated by electromagnetic radiations. Though molecules exhibit shorter spin coherence times than spin impurities in inorganic lattices, they have the advantage that their magnetic properties tuned through molecular synthetic strategies.<sup>1</sup> They can be designed to host several qubits with a precise control of their interaction allowing for the realization of quantum gates and quantum simulator.

Molecules can also be processed to be deposited on surfaces, allowing the realization of hybrid nanostructures and single molecule addressing through scanning tunnel microscopy. The latter has been recently employed to perform Electron Paramagnetic Spectroscopy on single atoms on a surface.<sup>2</sup> Though similar experiments are still unprecedented for molecules, the latter have also shown a tuneable interaction of the molecular spin with the Cooper pairs of an underlying superconducting thin film.<sup>3</sup> Organization of magnetic molecules on surface is also of relevance to achieve an electric control of the interaction between molecular spin qubits, as recently proposed to achieve scalability in silicon-based qubits. Our recent investigations employing electrically modulated EPR spectroscopy<sup>4</sup> have shown that the magnetic exchange interaction between molecular spins can be controlled by an electric field without relying on large spin-orbit coupling, and thus feasible in systems with long spin coherence times.

An overview of our recent results in the field will be presented here.

### References

1. (a) Gaita-Ariño, A., Luis, F., Hill, S., Coronado, E., *Nat. Chem.* **2019**, *11*, 301; (b) Atzori, M., Sessoli, R. *J. Am. Chem. Soc.* in press.
2. Baumann, S., Paul, W., Choi, T., Lutz, C. P., Ardavan, A., Heinrich, A. J., *Science* **2015**, *350*, 417.
3. Malavolti, L., Briganti, M., Hänze, M., Serrano, G., Cimatti, I., McMurtrie, G., Otero, E., Ohresser, P., Totti, F., Mannini, M., Sessoli, R., Loth, S., *Nano Lett.* **2018**, *18*, 7955
4. Fittipaldi, M., Cini, A., Annino, G., Vindigni, A., Caneschi, A., Sessoli, R., *Nat. Mater.* **2019**, *18* (4), 329.

## Putting a New Spin on Porphyrin Molecular Wires

Gabriel Moise,<sup>1</sup> Ashley J. Redman,<sup>1</sup> Lara Tejerina,<sup>2</sup> Michael Rickhaus,<sup>2</sup> Sabine Richert,<sup>1,3</sup> Claudia Tait,<sup>1,4</sup> Michael J. Therien,<sup>5</sup> Harry L. Anderson,<sup>2</sup> and Christiane R. Timmel<sup>1</sup>

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The custom synthesis of highly conjugated supramolecular assemblies has long been of paramount importance in driving the development of functional materials on a molecular scale. Within this lively and fast moving field of research, the chemical design of efficient molecular wires has been taking a central role with numerous applications in the fields of molecular electronics and photovoltaics.

Our laboratory has focused on the investigation of such molecular wire systems in their paramagnetic states, both in the cationic forms<sup>1</sup> and their photoexcited triplet states<sup>2</sup> using a variety of Electron Paramagnetic Resonance techniques in combination with Density Functional calculations to obtain information on the systems' geometries, magnetic parameters as well as crucial insights into the spin delocalization of the paramagnetic species.

The talk will commence with a summary of our present understanding of effects such as conjugation length, linker geometry and symmetry on spin delocalisation in these supramolecular structures before two projects are discussed in more detail: (1) the effects of donor-acceptor *meso* groups on Zero Field Splitting, hyperfine coupling and electron delocalization in a series of photo-generated triplet states of linear zinc porphyrin systems and (2) the limits of EPR linewidth analysis<sup>3</sup> in quantifying spin delocalization in ionic supramolecular structures.

### References.

1. M. D. Peeks et al. *J. Am. Chem. Soc.* **2017**, *139*, 10461.
2. C. E. Tait et al. *JACS* **2015**, *137*, 6670-6679; C. E. Tait et al. *JACS* **2015**, *137*, 8284-8293
3. J. R. Norris et al. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 625.

## Pulsed Dipolar Spectroscopy: From Model Systems to Cells

Olav Schiemann<sup>1</sup>

1) Institute of Physical and Theoretical Chemistry, University of Bonn, Germany

Understanding the function of biomolecules on a molecular level requires knowledge about their structure and conformational changes during function. Site directed spin labeling (SDSL) in combination with pulsed dipolar EPR spectroscopy (PDS) enables to gather such information on the nanometer length scale. In the talk, it will be shown that the SDSL/PDS approach enables the localization of metal ions within the fold of biomolecules,<sup>1</sup> including high-spin metal ions with large zero-field splitting<sup>2,3</sup> and low-spin ions with large g-anisotropy.<sup>4</sup> It will also be shown that this cannot only be done in vitro but also within cells.

In order to apply the SDSL/PDS approach within cells, a synthesis strategy for suitable trityl radicals and how to attach them in a site specific and highly efficient manner to proteins will be presented. Last but not least, an example will be given where a conformational change of a protein is followed with microsecond time resolution using PDS/SDSL.

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## **EPR and Industry applications**

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Likely something secret,

since the Abstract was not delivered.....

## EPR Spectroscopy of [FeFe] Hydrogenase H-Cluster Bioassembly Intermediates

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Radical SAM enzymes<sup>1</sup> use a [4Fe-4S] cluster to cleave S-adenosylmethionine to generate the 5'-deoxyadenosyl radical, which abstracts an H-atom from a given rSAM enzyme's substrate to initiate catalysis. In the maturation of the [Fe-Fe] hydrogenase H-cluster, the radical SAM enzyme HydG lyses tyrosine to generate the CO and CN ligands of the H-cluster of [FeFe] hydrogenase, ultimately building an organometallic Fe(CO)<sub>2</sub>CN(cysteine) moiety that incorporates an iron atom derived from a unique 5-Fe Fe-S cluster<sup>2-7</sup>. How these "synthons" are pairwise introduced into the formation of the H-cluster, along with the molecular and enzymatic origin of the azadithiolate bridge component of this catalytic cluster, are a current experimental focus of the laboratory. We are also revisiting details of the initial radical SAM tyrosine radical reactions<sup>2</sup> and trying to understand the yet unknown details of CN and CO formation and binding to the "dangler Fe" of the 5-Fe cluster with a combination of EPR and other spectroscopies along with computational chemistry.

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## Calculations and interpretation of the EPR parameters in the framework of 2- and 4-component DFT approach

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For more than 25 years Density Functional Theory (DFT) remains the “working horse” of the modern quantum chemistry. Despite its limitations DFT provides reasonable accuracy in calculations of parameters of NMR and EPR spectra. Still due to the richness of open-shell electronic systems there are many open questions in this field. One of the important issues is the interpretation of quantum-chemical results that provides further insight into experimental findings. Another challenging topic is a proper consideration of relativistic effects in calculations of EPR parameters for compounds containing heavy elements. In the current lecture some of these issues would be considered and analyzed.

Acknowledgment: This work received funding from the from the Slovak Research and Development Agency (grant APVV-15-0726).

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## Surface Chemistry and Catalysis by EPR: Concepts, Examples and Perspectives.

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

In this contribution, an overview of the wealth and breadth of information that can be obtained from EPR in the characterization of paramagnetic species in heterogeneous catalysts will be provided, illustrating the advantages that modern pulsed EPR methodologies can offer in monitoring the elementary processes occurring within the coordination sphere of surface transition-metal ions. Specific cases involving TMI acting as active catalytic sites will be presented, trying to outline the methodological approaches, which characterize the application of advanced EPR techniques and the questions that can be answered and addressed relative to the characterization of heterogeneous catalytic materials.

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## Bruker's latest EPR developments

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The presentation highlights the latest developments of Bruker in the field of EPR instrumentation. Major drivers of recent developments have been improvements in sensitivity, time resolution and data analysis tools.

Bruker's continuous efforts to improve EPR instrumentation in all aspects has led to the development of Rapid Scan. With the new Rapid Scan unit, very significant improvements in sensitivity and time resolution are achieved. In RS-EPR, the EPR absorption spectrum up to a width of 200 G can be acquired on a time scale of microseconds. Due to the short time during which the spins are exposed to microwave field, the saturation effect is less pronounced compared to conventional continuous-wave EPR. Thus, higher microwave fields can be used to increase the signal amplitude. In addition, Rapid Scan provides the opportunity for unprecedented levels of time resolution while collecting the EPR spectrum for following reaction kinetics by continuous-wave techniques.

In addition to the sensitivity gain in spectroscopy by Rapid Scan, the technique also offers a tremendous gain in spatial resolution in EPR imaging. First results of RS imaging at 1 GHz will be shown.

Significant gains in resolution and bandwidth have been achieved by the 3<sup>rd</sup> generation of SpecJet and video amplifier for the pulse EPR instrument E580. The improvements will be illustrated by examples.



## **Keynote Lectures**



## EPR-on-a-chip: A new paradigm in EPR spectroscopy

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2) Centre for Integrated Quantum Science and Technology (IQ<sup>ST</sup>)

3) Helmholtzzentrum für Materialien und Energie Berlin

CMOS-integrated, oscillator-based EPR detection was first introduced in <sup>1</sup> and extended to the use of voltage controlled oscillators (VCOs) in <sup>2</sup>. The VCO-based detection approach offers very interesting features such as the possibility of performing wide frequency sweeps with nearly constant sensitivity <sup>3</sup>, rapid scan EPR experiments with sweep rates as large as several GHz/ $\mu$ s <sup>4</sup> and dead time free pulsed EPR, including the unique feature of inductive detection during the pulse. Combined, these features render VCO-based EPR a very attractive alternative to conventional, resonator-based EPR detection. When a single VCO is used for detection, the excellent miniaturization capabilities of CMOS processes allow for the realization of detection coils as small as a few tens of micrometres, which offer outstanding spin sensitivities with built-in B1-sources up to very large frequencies beyond 100 GHz <sup>5</sup>. Moreover, the concentration sensitivity can be greatly improved by combining a large number of VCO-based detectors into injection locked arrays <sup>6</sup>. Interestingly, in this approach an array of  $N$  VCOs can be read out by a single readout variable, the joint array frequency.

In this keynote lecture, after a brief review of the basic concept and modelling of the VCO-based detection approach, we will discuss our latest prototypes that are targeting a wide range of applications from portable EPR to high-end spectrometry at hundreds of GHz.

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## EPR of metal-organic frameworks: from defects elucidation to new functionalities

Matvey Fedin,<sup>1</sup> Artem Poryvaev,<sup>1</sup> Daniil Polyukhov,<sup>1</sup> Eva Gjuzi,<sup>2</sup> .  
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Metal-organic frameworks (MOFs) are the promising nanomaterials for various applications, such as gas separation and storage, catalysis, etc. In many cases paramagnetic centers in MOFs play crucial role for their functionality, and such centers can be fruitfully studied by EPR. In particular, nanosized structural defects in MOFs attract growing attention, and the ways of their target generation and characterization are of significant interest. In this work we prepared and studied a series of MOFs based on copper(II) paddle-wheels with a new stable radical linker (derivative of the Blatter's radical) doped into the structure. CW/pulse EPR studies indicated that the radical linker binds to the copper(II) units differently compared to diamagnetic linker, resulting in the formation of nanosized structural defects. Moreover, remarkable kinetic phenomena were observed upon cooling of this MOF, where slow structural rearrangements and concomitant changes of magnetic interactions were induced. Thus, our findings demonstrated that doping of structurally-mimicking radical linkers represents an efficient approach for designing target defects and introducing new magnetostructural functionalities into MOFs.

Another promising application of MOFs is the separation of molecules with close dimensions and structures, such as various types of isomers. The efficiency of separation can be greatly enhanced if the apertures of the nanosized windows, allowing or prohibiting the diffusion of a particular molecule inside the cavities, are fine tuned by external stimuli. We report the new spin-probe EPR approach for precise measurement and controlled tuning of window sizes in ZIF-8 MOF and exemplify it by efficient separation of xylenes, which is of high practical importance. For this sake, stable nitroxides were entrapped in the pores of MOF for in-situ EPR kinetic measurement of the diffusion of various guest molecules through the material. Slight variation of temperature in conjunction with EPR control of molecular diffusion allowed tuning of the windows and reaching optimum conditions for ,separation of xylene isomers with the efficiency up to 92-95%.

This work was supported by RFBR (№ 18-29-04013).

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## First principles determination of EPR parameters in a triple decker of cerocene

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Quantum chemistry tools permit to describe the magnetic properties of f complexes. The large spin-orbit coupling and the semi-core character of the 4f and 5f orbitals confer to these molecules novel magnetic properties. Since a decade, there has been a large investigation of complexes with one magnetic center and first principles calculations have become an essential tool to interpret the experimental data, providing the nature of the ground state, the energy of exciting states and the corresponding directions of the magnetic moments.

Multiconfigurational methods provide the full knowledge of the wave function which permit to calculate the parameters of Spin Hamiltonians<sup>1,2</sup>. This will be exemplified by a double decker of cerocene and its triple decker counterpart<sup>3</sup> (see Fig. 1) which were fully characterized by EPR by Walter et al.<sup>4</sup>

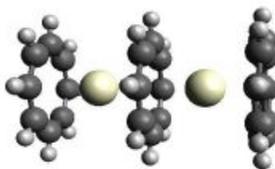


Figure 1. [Ce COT<sub>3</sub>]<sup>2-</sup>

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## Light-induced pulsed EPR dipolar spectroscopy: the triplet state probe

Maria Dal Farra<sup>1</sup>, Susanna Ciuti<sup>1</sup>, Alice M. Bowen<sup>2</sup>, Sabine Richert<sup>2</sup>,  
Christiane R. Timmel<sup>4</sup>, Stefan Stoll<sup>3</sup>, Marina Gobbo<sup>1</sup>, Donatella Carbonera<sup>1</sup>  
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Light-induced pulsed EPR dipolar spectroscopy (PDS) allows the determination of nanometer distances between paramagnetic sites, employing as orthogonal spin labels a chromophore triplet state and a stable radical.<sup>1,2</sup> The distinctive properties of the triplet state, *in primis* the spin polarization enhancement of the EPR signal and the photoinduced behavior of the spin probe, have been successfully exploited.

The versatility of this methodology is ensured by the employment of different techniques: in addition to double electron electron resonance (DEER/PELDOR), relaxation-induced dipolar modulation enhancement (RIDME) is applied for the first time to the photoexcited triplet state. An alternative pulse scheme for laser-induced magnetic dipole (LaserIMD) spectroscopy, based on the refocused-echo detection sequence, is proposed for accurate zero-time determination and reliable distance analysis.<sup>3</sup> These techniques complement each other and, depending on the nature of the triplet spin label, they can be used interchangeably to take advantage of specific characteristics, selecting the pulse sequence that yields the best performance for the system of interest.

Light-induced PDS has been applied on a peptide-based spectroscopic ruler<sup>2</sup> in order to test the accuracy, sensitivity and distance limits and extended to paradigmatic proteins in order to prove the feasibility of distance measurements using endogenous triplet state probes found in different classes of proteins.<sup>3,4</sup>

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

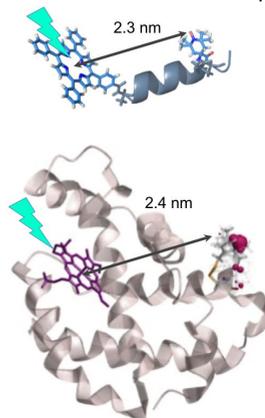


Figure 1. Top: Peptide-based model system containing a porphyrin chromophore a TOAC nitroxide. Bottom: a protein containing an endogenous porphyrin and singly labelled with MTSSL.

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## Protein film electrochemical EPR spectroscopy as a technique to investigate redox reactions in biomolecules

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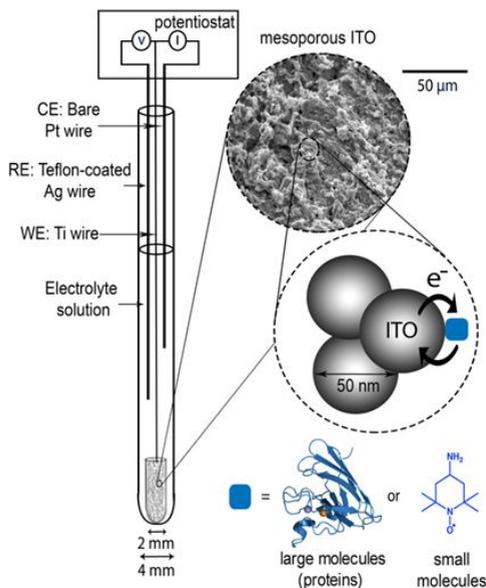
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Redox reactions and paramagnetic intermediates are ubiquitous in biological chemistry. The usefulness of combining EPR and electrochemistry to access both detailed information on redox processes and structures of paramagnetic states in order to gain mechanistic understanding of chemical reactions is well-recognised, with the first experiments dating back to the 1970s.<sup>1,2</sup>

We report a new method, protein film electrochemical EPR (PFE-EPR), that enables direct (non-mediated) and accurate potential control of proteins on the electrode surface for both electrochemical and EPR spectroscopic characterisation of their redox centres.

Experiments with the stable redox-active radical (4-amino-TEMPO) and the enzyme Cu-Zn superoxide dismutase (SOD) demonstrate that PFE-EPR is not only feasible but provides astonishing sensitivity, which is attributed to the highly porous tuneable working-electrode material to which the redox-active molecules are attached.<sup>3</sup>



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## Membrane transport explored with pulsed ESR spectroscopy

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Membrane proteins often sample a broad conformational landscape and the activity of channels, transporters, or receptors often involves large-scale domain movements. Thus, a mechanistic understanding of their function requires the characterization of conformational changes, equilibrium dynamics, intermediate states, and the thermodynamic parameters. The dream for a structural biologist would be to observe the above phenomena in the native environments. Pulsed ESR spectroscopy has emerged as a versatile tool for membrane protein structural biology. We have shown that PELDOR can monitor ligand-induced conformational equilibrium as well as a previously uncharacterized intermediate state in the ABC exporter TmrAB.<sup>1</sup> Also, under favourable circumstances the thermodynamic parameters for the conformational switching can be determined. When a membrane protein oligomerize exclusively in the lipid environment, the structure determination is a challenging task. For the proton-coupled fumarate symporter SLC26Dg, we determined the dimer structure in proteoliposomes using PELDOR constraints. Rigid-body docking using either the time-domain data or the interspin distances revealed a novel interface, which could be further validated with cysteine cross linking in the native membranes.<sup>2</sup> Furthermore, the structure and the conformational changes in outer membrane transporters has been observed in both intact *E. coli* and native outer membranes using PELDOR.<sup>3,4,5,6</sup>

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## Endohedral spins in carbon cages

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Carbon cages known as fullerenes are able to encapsulate various metal atoms and stabilize unusual species within their interior. Protected by the fullerene cage, the endohedral clusters often exhibit unconventional valence and spin state and interesting magnetic properties. Metal-fullerene interactions are usually characterized by a transfer of metal valence electrons to the carbon cage. However, for Sc, Y, and some lanthanides, the energy of the  $\sigma$ -type M–M bonding orbital in  $M_2$  dimers encapsulated within the fullerene cage is often rather low, which limits the  $M_2 \rightarrow$  fullerene transfer to only five electrons. This leads to the appearance of a metal–metal bonding orbital occupied with one electron. An air-stable form of such dimetallofullerenes have been obtained as benzyl monoadducts  $M_2@C_{80}(CH_2Ph)$  ( $M = Sc, Y, Gd-Er$ ).<sup>1,2</sup> Due to the presence of M–M bonding molecular orbital with one electron,  $M_2@C_{80}(R)$  molecules feature a unique single-electron M–M bond and unconventional +2.5 oxidation state of Sc, Y, and lanthanides. The unpaired electron residing on the M–M bonding MO acts as a radical bridge (Fig. 1), leading to giant exchange coupling between local lanthanide moments. Besides, since the metal–metal bonding orbital has large contribution from s-atomic orbitals of metals, for Sc and Y analogs this situation leads to the giant hyperfine coupling. In this contribution we will discuss spin properties of such dimetallofullerenes with the special focus on their EPR studies.

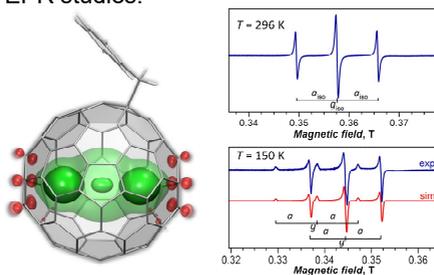


Figure 1. Spin density distribution in  $Gd_2@C_{80}(CH_2Ph)$  (left) and EPR spectra of  $Y_2@C_{80}(CH_2Ph)$  measured at room temperature and in frozen solution (right)

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## **Oral Presentations**





## Magneto-Structural Correlations in Six- to Two-Coordinate Cobalt Complexes with Large Magnetic Anisotropies

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Molecular nanomagnets (MnMs) exhibit fascinating magnetic properties with relevance to potential applications like magneto-caloric cooling, single molecule based data storage, quantum computing and other spintronics applications. A key property to control and understand MNM properties is their magnetic anisotropy. It is determined by the coordination environment and can be quantified by EPR measurements. However, the relevant energies span several orders of magnitude. The present study therefore relies on a combination of very broadband Frequency-Domain Fourier-Transform THz-EPR (FD-FT THz-EPR)<sup>1</sup> and conventional multi-frequency (S-, X-, Q-band) EPR techniques.

Co(II) complexes are an ideal platform for knowledge based MNM design strategies. Co(II) frequently exhibits large first order spin-orbit coupling (SOC) resulting in very large magnetic anisotropies. Due to rapid progress in quantum chemical calculation methods, these properties are increasingly well understood and can be predicted by magneto-structural correlations. Inversely, experimentally obtained anisotropies are an important benchmark for state-of-art-quantum chemical calculations.

Herein, we present EPR experiments on different six-, four-<sup>2-3</sup> and two-coordinate Co(II) MNMs, exhibiting zero field splittings with energies in the range from 40 to 300 cm<sup>-1</sup>. For each of these complexes, experimentally obtained magnetic anisotropies are complemented by quantum chemical calculations. In addition, different approaches to fine-tune magnetic anisotropy by ligand exchange, exchange of the counter ion and subtle changes of the host matrix of the complex are presented and discussed.

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## Binding of tetracycline to its aptamer determined by 2D-correlated Mn<sup>2+</sup> hyperfine spectroscopy

Thilo Hetzke<sup>1</sup>, Alice M. Bowen<sup>2</sup>, Marc Vogel<sup>3</sup>, Maximilian Gauger<sup>1</sup>,  
Beatrix Suess<sup>3</sup>, Subham Saha<sup>4</sup>, Snorri Th. Sigurdsson<sup>4</sup> and  
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Recently, the pulsed hyperfine technique ELDOR-detected NMR (EDNMR) was shown to be applicable at Q-band frequencies (34 GHz).<sup>1</sup> In previous studies, EDNMR was mostly used at W-band frequencies (94 GHz), as here the central blindspot does not obscure nuclear frequencies.

In the present study,<sup>3</sup> we use EDNMR- and also ENDOR-based hyperfine methods to investigate the Mn<sup>2+</sup>-mediated binding of the antibiotic tetracycline (TC) to a tetracycline-binding RNA aptamer (TC-aptamer).<sup>4</sup>

Conventional Mn<sup>2+</sup> 1D-hyperfine studies show two distinct <sup>31</sup>P-hyperfine couplings besides a pronounced <sup>13</sup>C signal originating from <sup>13</sup>C labeled TC. Based on these data alone, however, it cannot be concluded if TC actually binds via Mn<sup>2+</sup> to the aptamer at physiological divalent metal ion concentrations. We therefore used 2D-correlated hyperfine techniques<sup>5</sup> to correlate <sup>31</sup>P (RNA) and <sup>13</sup>C (TC) nuclei to the same Mn<sup>2+</sup> electron spin, thus confirming the formation of a ternary RNA-Mn<sup>2+</sup>-TC complex. 2D-EDNMR showed to be much more sensitive than THYCOS (triple hyperfine correlation spectroscopy), albeit analysis of 2D-EDNMR data is hampered by a reduced spectral resolution. Out of the two observed <sup>31</sup>P hyperfine couplings, only the smaller coupling shows a clear correlation to the <sup>13</sup>C nucleus. THYCOS was also used to determine the sign of the <sup>13</sup>C hyperfine coupling.

Additional Mn<sup>2+</sup> binding sites of the aptamer and their importance for folding of the RNA are identified by performing nitroxide-Mn<sup>2+</sup> PELDOR and comparing the extracted distances to the ones from the crystal structure.<sup>5</sup> First Mn<sup>2+</sup> titration studies of a singly labeled nitroxide aptamer with varying Mn<sup>2+</sup> concentrations in the absence and presence of TC will be presented.

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## Combined EPR and ODMR approach to study degradation of fullerene-free organic solar cell materials

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Organic solar cells (OSCs) represent an environmentally friendly technology that shows a great promise in solar energy conversion. The active layer of such a device consists of nanoscale interpenetrating regions of electron donor and acceptor molecular materials, forming the so-called bulk heterojunction (BHJ). Despite recent advances in devices performance (PCEs over 15%) and material synthesis, the long-term stability of OSCs still remains a major problem.<sup>1</sup> We present here an investigation of photodegradation in fullerene-free OSC materials, the blend of the workhorse donor polymer P3HT and the rhodamine-flanked acceptor small molecule FBR.<sup>2</sup>

Electron paramagnetic resonance (EPR) is used in the X- and W-band to analyze the radicals ( $S = 1/2$ ) generated in pure P3HT and in the P3HT:FBR blend under illumination in the absence and presence of oxygen. Apart from the positive charge carrier in P3HT, called positive polaron, the production of the previously reported complex  $[P3HT:O_2]^-$  of a weakly bound superoxide on the polymer was confirmed in degraded pure P3HT but also in the degraded P3HT:FBR blend.<sup>3</sup> In the undegraded blend, the negative charge carrier in FBR, or negative polaron  $P^-$ , was observed after low-temperature light excitation. Its spectrum can be unequivocally distinguished from the overlapping  $[P3HT:O_2]^-$  spectrum by ELDOR-detected NMR. Triplet excitons (TEs), carrying spin  $S = 1$ , can be created after photoexcitation by intersystem crossing and found to be involved in material photodegradation by energy transfer towards  $O_2$  molecules generating reactive singlet excited state  $^1O_2$ . The TEs are monitored in both P3HT and FBR by means of optically detected magnetic resonance (ODMR). The ODMR of TEs is strongly quenched in P3HT:FBR owing to efficient charge separation in this blend. While the TEs spectrum is expected to reappear in both materials under photodegradation, due to reduction in charge separation efficiency, only the FBR signature was observed. The correlation will be discussed between the efficient charge separation, the quenching of the TE ODMR spectrum in the blend and the observation that the FBR molecule is less vulnerable in the P3HT:FBR blend than in the pure FBR film. Finally, we employ a spin trapping technique to confirm degradation pathway via sensitization of  $^1O_2$ .

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## EPR probes two closed ATP/ADP conformations and small nucleotide-driven structural changes in yeast Hsp90 chaperone

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Hsp90 is an important molecular chaperone conserved from bacteria to mammals that prevents misfolding of proteins directly associated with cancer and neurodegenerative diseases.<sup>1</sup> In terms of structure, Hsp90 is a large flexible homodimer (180 kDa), constitutively dimerized at the C-termini. Hsp90 consumes energy from ATP together with Mg(II) ions as co-factors. The ATPase site is in both N-termini and the ATPase cycle is accompanied by large global conformational changes, which involve transition from a nucleotide-free 'open' to an ATP-bound 'closed' conformation *via* dimerization of the N-termini.<sup>1</sup> However, it is under debate whether the post-hydrolysis (ADP-bound state) is 'open' or 'close'.

We address this question by investigating the local structural changes at the ATPase site and the concomitant conformational changes at various nucleotide-bound states in yeast Hsp90 using EPR techniques. First, using site-directed spin labelling (SDSL) with nitroxide and Gd(III) labels and DEER we monitored inter-monomer rearrangements at different states of the ATPase cycle. We, also, substituted Mg(II) with Mn(II) and performed hyperfine and pulse dipolar EPR. Specifically, we tracked the ATP hydrolysis using <sup>31</sup>P ENDOR and investigated Mn(II)-protein interactions by <sup>14/15</sup>N EDNMR. We, also, measured the distance between the Mn(II) cofactors using DEER/PELDOR spectroscopy.

We observed large disorder of Hsp90 as well as spin label flexibility and found that the presence of nucleotide merely dictates the conformational ensemble. This is in contrast to a well-defined Mn(II)-Mn(II) distance in the ATP state, which shortened and broadened in the ADP state, providing experimental evidence to the existence of two different 'closed' conformations. The exploitation of the intrinsic metal binding site allowed us probe local and global interactions from a single sample and obtain new structural insights previously challenging to observe with other techniques. DEER on mutants revealed small nucleotide-driven structural preferences implying the role of co-chaperones and/or substrates to be the trigger for large conformational changes.

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## EPR Spectroscopy of f-Block Organometallic Compounds

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Spin-echo techniques enable characterization of molecular quantum states, as well as measuring quantum coherence and spin entanglement in multi-qubit arrays.<sup>1,2</sup> A requirement for quantum bits (qubits) is to have long memory times to avoid loss of information.

The focus of current strategies is the engineering of nuclear spin-free environments, believed to mediate spin decoherence. The task is very challenging. Here we show that sufficiently long phase memory times enabling quantum spin manipulations even at room temperature are achievable in cyclopentadienyl f-element complexes that are rather rich in nuclear-spins. For the family of compounds LnCp<sub>3</sub>K, with Ln = Sc, Y, La or Lu, coherent Rabi oscillations were measured up to 300 K in a single crystal. Ac magnetic susceptibility data confirmed slow magnetic relaxation at low temperatures, associated with very long spin lattice relaxation times. Despite many <sup>1</sup>H and <sup>13</sup>C nuclei present, all electronuclear transitions of the compounds enabled to be coherently manipulated (Figure 1), indicative that the qubit memory time is protected in these systems due to a reduced orbital angular momentum of the ground spin state. We took advantage of these properties to measure actinide covalency via pulsed EPR methods (HYSCORE), for the first time.<sup>3</sup>

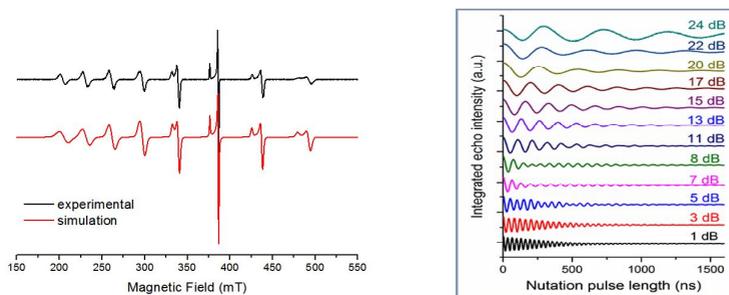


Figure. 1 Cw-EPR spectrum (left), and Rabi oscillations (right), for Lu(Cp<sub>3</sub>)K.

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## Strain Effects of <sup>31</sup>P Hyperfine Coupling Constants in the Conformationally Flexible [Cu{Ph<sub>2</sub>P(O)NP(O)Ph<sub>2</sub>}<sub>2</sub>] Complex, as Revealed by HYSORE Spectroscopy

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Strain effects on  $g$  and metal hyperfine coupling tensors,  $A$ , are often manifest in EPR spectra of transition metal complexes, as the result of their intrinsic and/or solvent-mediated structural variations.<sup>1</sup> Although distributions of these tensors are quite common and well understood in cw EPR spectroscopy, reported strain effects on ligand hyperfine coupling constants are rather scarce.<sup>2,3</sup> Here we explore the case of [Cu{Ph<sub>2</sub>P(O)NP(O)Ph<sub>2</sub>}<sub>2</sub>], a square-planar Cu(II) complex bearing P atoms in its second coordination sphere.<sup>4</sup> The HYSORE spectra of this complex exhibit correlation ridges that have unusual inverse or so-called “boomerang” shapes and features that cannot be reproduced by standard simulation procedures assuming only one set of magnetic parameters. Our work shows that a distribution of isotropic hyperfine coupling constants spanning a range between negative and positive values is necessary in order to describe in detail the unusual shapes of these HYSORE spectra. Moreover, by employing DFT calculations, we demonstrate that lineshape analysis of such HYSORE spectra provides new insight into the structural dynamics of the spin system under investigation.

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## The Bifunctional Chemistry of Bis(acyl)phosphane Oxides in Aqueous and Alcoholic Media

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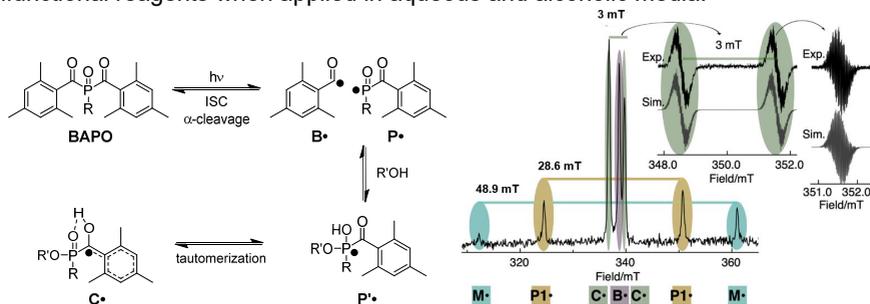
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In this contribution, the remarkable photochemistry of bis(acyl)phosphane oxides (BAPOs), a widely employed class of radical photoinitiators, is presented: Photolysis of BAPOs in the presence of water or alcohols provides a new delocalized  $\pi$ -radical, which does not participate in polymerization reactions. We have established the structure and reactivity of this  $\pi$ -radical using steady-state and time-resolved (CIDEP) EPR together with ESI-MS, NMR spectroscopy, and DFT calculations: The new radical species either converts into a mono(acyl)phosphane oxide acting as a secondary photoactive species or acts as a one-electron reducing agent. Upon the electron-transfer process it again produces a dormant photoinitiator. These results show that bis(acyl)phosphane oxides act as bifunctional reagents when applied in aqueous and alcoholic media.<sup>1</sup>



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## Nitroxide spin labeling with copper click chemistry

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EPR spectroscopy in combination with site-directed spin labeling (SDSL) is an important tool to obtain long-range distance restraints for protein structural research. There is a need for the development of new labeling strategies, as many research questions are not accessible with conventional cysteine-based approaches. Additionally, in the light of recent advances in the field of in-cell EPR spectroscopy, linker stability, as well as bioorthogonality of the labeling reaction, need to be taken into consideration.

We are therefore working on a nitroxide-based spin labeling approach that utilizes the incorporation of noncanonical amino acids (ncAA) into a given protein, followed by label attachment via copper-catalyzed azide-alkyne cycloaddition (CuAAC). In a comparative study<sup>1</sup>, we tested a variety of azide and alkyne-bearing ncAA in terms of protein single- and double-incorporation efficiency via nonsense suppression, metabolic stability, and yields of nitroxide labeling via CuAAC. We evaluated the spectroscopic properties of the resulting linkages in continuous-wave and DEER measurements.

CuAAC-based SDSL with suitable ncAA will increase the range of available nitroxide spin labels and may prove particularly useful in cases in which essential cysteines of a target protein prevent the use of sulfhydryl-reactive spin labels. Moreover, the labeling reaction is bioorthogonal and may prove useful in in-cell EPR spectroscopy.

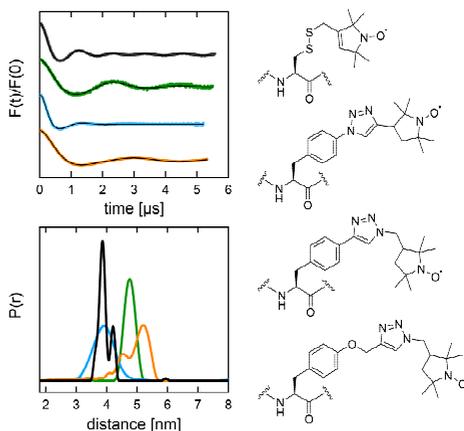


Figure 1. Chemical structure of nitroxide labels with various linkages and the derived DEER data upon double-labeling of the model protein Thioredoxin at position 14/34.

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## **Electrostatics in Solid-Supported Lipid-Protein Systems**

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Design of new bio-nano hybrid systems calls for understanding and accounting for the influence of a nanostructured support and nanoconfinement on the structure and biophysical properties of lipid bilayer hybrid systems and membrane-protein interface. Here we report on spin-labeling EPR studies of pH-sensitive lipids and specifically labeled protein side chains to assess effects of solid inorganic interface, specifically, silica support in a form of monodispersed nanoparticles ranging from 20 to 300 nm in diameter on the surface electrostatic potential of lipid bilayers associated with the particles and effective pKa of the membrane-buried peptide ionisable sidechains. We have shown that bilayers formed from zwitterionic or mixed (positively or negatively charged and cholesterol) lipids on silica nanoparticle surfaces possess a higher negative electrostatic potential than the unsupported bilayers with the potential of mixed bilayers containing negatively charged lipids being significantly more sensitive to the silica support. Effect the silica nanoparticle size on the lipid bilayer surface electrostatic potential was also observed for particles smaller than 100 nm. Addition of cholesterol to the phospholipid bilayers reduced but not diminished the effect of support. pH-sensitive EPR probes were then employed to label model WALP peptide known to form an  $\alpha$ -helix when integrated into a lipid bilayer. The silica support exerted pronounced effects on WALP dynamics and the effective pKa of the ionizable probe. It was demonstrated that the silica nanoparticles shift the effective pKa of the ionizable nitroxide probe in a membrane depth-dependent manner. Upon protonation of the membrane-buried model ionisable sidechain the silica support caused significant changes in the membrane association of WALP peptide that are not observed when WALP is integrated into unilamellar phospholipid vesicles of similar curvature. Supported by NSF 1508607 to TIS.

## Microtubule (MT) Binding Domain of tau protein studied by cw-ESR and pulsed ESR analysis

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Tau is a microtubule(MT)-associated protein that is involved in neurodegenerative tauopathies and dementia, especially Parkinson's and Alzheimer's disease. In Alzheimer's disease, the disaggregation of MT (bundles of tubulin) is one of the first steps leading to malfunction of the brain. Understanding how Tau protein helps to stabilize the MT is crucial to find a cure for these neuropathies.

Tau protein belongs to the intrinsically disordered protein family. This results in difficulties to study its structure by usual techniques (NMR, XRD). Recently, 3D Cryo-EM image reconstructions were obtained by Kellogg et. al.<sup>1</sup> to reveal information on the association of tau with MT (see Fig.1). **In this work, we aimed to detect, in the liquid state, the dynamic changes in the structure of tau upon binding to microtubules by employing Electron Spin Resonance (ESR) techniques.**

A first study by cw-ESR and pulse dipolar spectroscopy (DEER) was conducted by Georgieva et. al.<sup>2</sup>, which focused on the interaction of tau with lipid membranes. In this new study, we directly explored the interaction of tau with microtubules in vitro. A site-directed spin labeling (SDSL) method was employed and a series of different cysteine mutants were expressed, and spin-labeled around the hexapeptide pair helical filament area (PHF6) of tau. The spin-labeled proteins were then mixed with the tubulin to express the MT. A change in the conformation of tau with the spin label residue position was deduced by cw-ESR lineshape analysis and by time relaxation measurements using pulse ESR techniques. This work is supported by NIH grant R01GM123779.

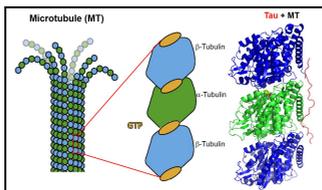


Figure 1. Proposed model of the association of Tau protein (in red) with the microtubules. (This figure was adapted from Kellogg et al.<sup>1</sup>, PDB file = 6CVN).

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## In vivo extracellular pH mapping of tumor mouse models using EPR

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A method of 3D extracellular pH ( $pH_e$ ) mapping of tumors using EPR is introduced.<sup>1</sup> For in vivo pH mapping, we used a pH-sensitive nitroxyl radical probe (dR-SG) and a 750-MHz home-built CW-EPR spectrometer/imager.<sup>2,3</sup> 4D spectral-spatial imaging was employed. After reconstructing EPR spectra at each voxel, the spectral data were converted to the value of pH. Known-pH solution samples were measured to demonstrate the accuracy and precision of pH mapping. The precision (functional resolution) of pH mapping was 0.078 pH units, and the accuracy was 0.026 pH units. Murine squamous cell carcinoma (SCC VII) models were prepared to monitor the progress of acidification of tumors.  $pH_e$  mapping of tumor-bearing mouse legs was conducted at five and eight days after SCC VII cell implantation to mouse hind legs. Moreover, we visualized  $pH_e$  for different tumor xenograft mouse models of human-derived pancreatic ductal adenocarcinoma cells (MIA PaCa-2, SU.86.86, and Hs766t).<sup>4</sup> This demonstrated 3D  $pH_e$  mapping method can quantitatively visualize the progress of acidification during tumor growth and different levels of acidification in different tumors.

Acknowledgement: This work was supported in part by JSPS KAKENHI Grants JP26249057 and JP18KK0304, Ministry of Education and Science of the Russian Federation grant 14.W03.31.0034, and NIH Grants CA194013 and CA192064.

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## A unique dual-mode microwave EPR reactor-resonator for T-jump experiments

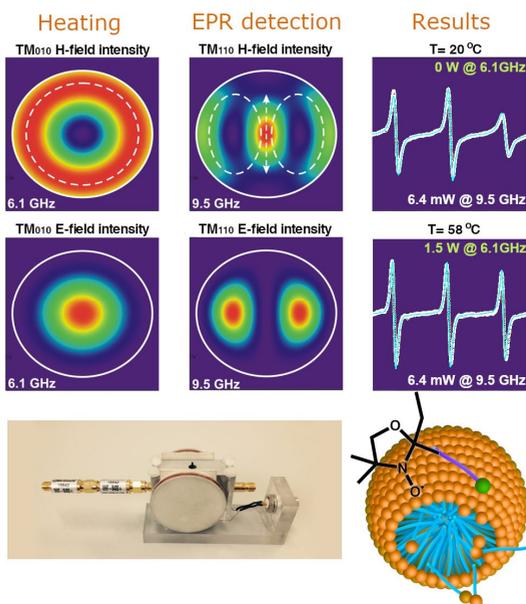
Andrea Folli<sup>1</sup>, Heungjae Choi<sup>2</sup>, Michael Barter<sup>2</sup>, Jaafar Harari<sup>2</sup>, Emma Richards<sup>1</sup>, Daniel Slocombe<sup>2</sup>, Adrian Porch<sup>2</sup>, Damien M. Murphy<sup>1</sup>

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We report here on the first stage of development of a unique dual-mode microwave (MW) EPR reactor-resonator (DMRR) for rapid MW perturbation/T-jump heating. Chemical reactions subject to a flow of energy and matter can be perturbed away from the thermodynamic equilibrium by imposing a rapid shock or physical change to the system. Depending on the magnitude of the perturbation, these changes can dictate the subsequent evolution of the entire system, allowing for instance to populate non-equilibrium reactive intermediate states. Most T-jump experiments are based

on Joule Heating (requiring a conducting solution) or IR lasers (requiring a solvent with strong IR absorption properties). Here we use microwaves, which offer an incredibly effective means of rapid, volumetric heating of a solution via electric dipole absorption. Our key concept is the use a DMRR based on a cavity resonator affording EPR detection (using a 9.5 GHz mode) at the same time as heating (using a 6.1 GHz mode excited with up to 10 W of microwave power). Temperature jumps of 50 °C in a few seconds are possible. The proof of concept described in this first account involved probing the temperature-induced variation of rotational dynamics of the 16-doxyl stearic acid methyl ester (16-DSE) spin probe grafted on the surface of sodium dodecyl sulphate (SDS) micelles. Our DMRR has the potential to interrogate paramagnetic intermediates relevant to catalysis, alter the product distribution and thereby enhance the abundance of thermodynamically unfavoured species, as well as study the kinetics of thermally driven spin crossover events if the T-jump shock is rapid enough.



## Methodological advances of W-band DEER with shaped pulses

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The DEER (double electron-electron resonance, also called PELDOR) experiment, which probes the dipolar interaction between two spins and thus reveals distance information, is an important tool for structural studies. In recent years, shaped pump pulses have become a valuable addition to the DEER experiment. Shaped pulses offer an increased excitation bandwidth and the possibility to precisely adjust pulse parameters, which is beneficial especially for demanding biological samples.<sup>1,2,3</sup> In our lab, we are employing an Arbitrary Waveform Generator (AWG) connected to our home-built W-band (95 GHz) EPR spectrometer to shape the DEER pump pulse and, doing so, significantly increasing excitation bandwidth and signal-to-noise ratio (SNR). Our recent advances include the use of a slightly modified DEER sequence titled rDEER4 that we use to circumvent a problematic coherence pathway which introduces artefact at the end of the DEER trace, and an increase in Gd(III)-Gd(III) DEER SNR in the range of 3-7, depending on the sample and the Gd(III) label used, when comparing DEER with shaped pulses to DEER with monochromatic pulses. This significant increase in SNR recently enabled us to perform a study on the membrane protein MdfA which suffers from short phase memory time and can be stabilized in detergent only at relatively low concentrations. We demonstrate the feasibility of this approach for Gd(III)-Gd(III) DEER on a variety of model proteins and with different spin labels. Additionally, we demonstrate the application of shaped pulses to trityl-based DEER, where precisely optimized pump pulses are beneficial for avoiding orientation selection effects.

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## OPERA: Out of Phase Experiment RIDME Application.

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EPR Pulsed Dipolar Spectroscopy techniques, such as **Relaxation Induced Dipolar Modulation Enhancement** (RIDME) and **Double Electron Electron Resonance** (DEER also known as PELDOR)<sup>1</sup>, are important techniques for structural determination. Both RIDME and DEER traces include a modulated dipolar component and a background function, containing an unmodulated component, an intermolecular interaction component and in the case of RIDME a relaxation component. The form of this background may be unknown, making it difficult to remove during analysis.

Out of Phase DEER methods have previously been reported aimed at minimizing the background component and also providing two synchronous data sets that can facilitate removal of the background function without knowing the exact form<sup>2</sup>. More recently, **Refocused Out Of Phase** (ROOPh) DEER, where in an additional group of pulses is used to remove the in-phase and refocus the out-of-phase component of the signal, has been published<sup>3</sup>.

Here we expand the application of refocused out-of-phase methodologies to the RIDME experiment; **Out of Phase Experiment RIDME Application** (OPERA). This is shown to successfully filter the unmodulated component of the RIDME signal and refocus the out-of-phase component of the signal for a nitroxide bi-radical (Fig. 1) and other model systems.

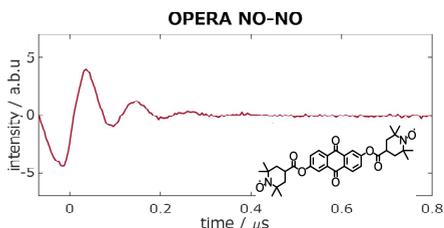


Figure 1. Experimental OPERA trace measured for a nitroxide bi-radical.

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## Excitation and readout of methyl group tunnel state coherence by pulse EPR spectroscopy

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At temperatures low enough to freeze out classical motion, methyl group quantum rotors undergo tunnelling. Their states are characterized by a tunnel splitting that depends on the height of the rotational barrier. The influence of tunnelling on methyl proton hyperfine couplings has long been observed by ENDOR and has served as an indirect probe of the tunnel splitting. Concomitant electron-nuclear spin flips that are the basis of ESEEM spectroscopy are considered “forbidden” in EPR spectroscopy. Canonically, their transition moments and hence intensities are magnetic field-dependent.

In contrast, we observed<sup>1</sup> magnetic field-independent “forbidden” transitions by ESEEM and here assign them as a direct observation of the hyperfine-perturbed methyl proton tunnelling splittings. Using site-specific deuteration, we identified the methyl groups of a dimethylammonium cation in a dense Mn(II)-doped metal-organic hybrid perovskite framework as the origin of these field-independent transitions. The vicinity of the electron spin breaks the  $C_3$  symmetry of the methyl groups, which here induces a polarization transfer to the tunnel splitting transition with an efficiency independent of the static magnetic field. By excitation of the electron spin with microwave pulses, we show that the tunnel-split states can be coherently superimposed and the phase of this coherence can subsequently be read out via the electron spin. The resulting ESEEM signals and spectra are in good agreement with predictions from simulations of the spin and tunnel-state dynamics and the observed tunnel splitting frequencies agree reasonably well with DFT calculations of the rotational barrier height.

These results pave the way to further study coherence transfers involving methyl group tunnel-split states and we discuss potential applications for dynamic nuclear polarization.

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## The electronic structure of the H-cluster in [FeFe] hydrogenase as analyzed through Q-band <sup>13</sup>C ENDOR spectroscopy. Implications for the catalytic mechanism.

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[FeFe] hydrogenases are the most active hydrogen converting enzymes in nature. Their active site contains a classical [4Fe-4S] cluster connected through one of the coordinating cysteines to a unique binuclear iron cluster [2Fe]<sub>H</sub> coordinated by CN<sup>-</sup> and CO ligands as well as a bridging aza-propane-dithiolate (ADT) ligand. The CN<sup>-</sup> and CO ligands keep the iron core in a low oxidation state (Fe(I) or Fe(II)) while the amine in the ADT ligand provides proton exchange functionality near the open coordination site at the distal iron Fe<sub>d</sub> where hydrogen splitting/formation occurs. Using EPR and NMR spectroscopy we obtained a detailed picture of the spin distribution over the H-cluster in its various redox states.<sup>1-3</sup> It turns out that the magnetic exchange interaction between the two sub-clusters leads to strong spin delocalization over the whole H-cluster as reflected in the observed <sup>57</sup>Fe hyperfine interactions for the active oxidized state H<sub>ox</sub> and the CO inhibited state H<sub>ox</sub>-CO. <sup>13</sup>C triple ENDOR experiments on an H-cluster in which the ADT ligand was isotope labeled revealed spin polarization in the ADT ligand coordination sphere. DFT calculations reproduce the magnetic properties of the ligand sphere such as the ADT moiety. The origin of the observed asymmetric spin distribution over the ADT ligand is related to the specific CO/CN sphere of the H-cluster. Furthermore, <sup>13</sup>C triple ENDOR experiments on the <sup>13</sup>CN labeled H-cluster in the CO inhibited state help to resolve a controversy concerning the ligand arrangement in this state. This study demonstrates that advanced pulsed EPR spectroscopy can provide both structural and functional information on the active site of [FeFe] hydrogenase thus helping to understand its catalytic mechanism.

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## Contactless millimeter wave method for quality assessment of large area graphene

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We demonstrate that microwave absorption experiments performed at our High Frequency EPR spectrometer<sup>1</sup> offer a route for efficient measurements of transport properties for fast and accurate quality control of graphene.<sup>2</sup> This contactless characterization method can be used to quickly evaluate transport properties over large areas without recourse to complex lithographic methods making it suitable as a probe of quality during wafer scale fabrication. In particular, we demonstrate that absorption measurement of transport properties is sensitive to inhomogeneities in sample transport properties. This is in contrast to traditional methods using electrical contacts which tend to overestimate transport properties due to the formation of preferential conducting channels between the electrodes. Here we compare Shubnikov–de Haas oscillations simultaneously detected by microwave absorption and by conventional contact Hall bar measurements in fields up to 15 T on quasi-free standing, large area (25 mm<sup>2</sup>) monolayer graphene. We find that although the evaluated charge carrier densities from both measurements are similar, the mobility differs considerably due to electronic transport inhomogeneity. Furthermore, our recent development of High Frequency EPR technique will be outlined.

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## Magnetolectric coupling in spin triangles

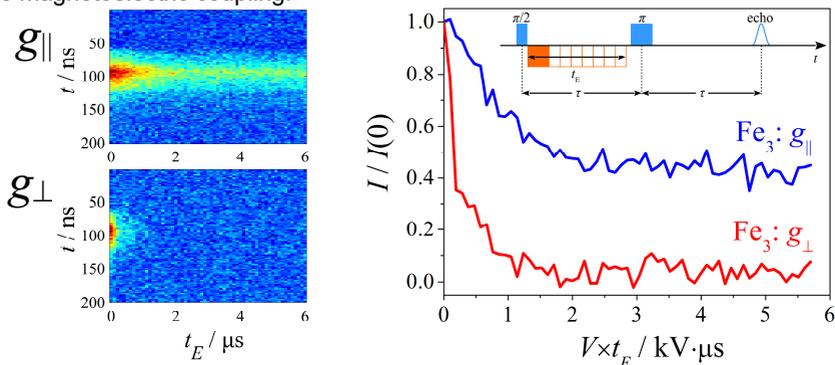
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Antiferromagnetic molecular triangles of half-integer spins, or “spin triangles”, have recently attracted renewed interest due to their proposed use as electrically controlled and slow-decoherence spin-chirality qubits.<sup>1</sup> Electric control of magnetic objects is expected to revolutionize spintronic applications, and has been reported in only a few classes of materials. The factors that determine the strength of magnetolectric coupling in exchange-coupled molecular materials are still poorly understood as very few such cases have been reported. Using CW-EPR spectroscopy, we recently reported the magnetolectric coupling in  $[\text{Fe}_3\text{O}(\text{PhCOO})_6(\text{py})_3](\text{ClO}_4)\cdot\text{py}$  (**1**) under static electric fields<sup>2</sup> while similar reports have been made using pulsed<sup>3</sup> or modulated electric fields.<sup>4</sup>

In this report we describe comparative studies of **1** and of closely related  $[\text{Cr}_3\text{O}(\text{PhCOO})_6(\text{py})_3](\text{ClO}_4)\cdot 0.5\text{py}$  using CW and pulsed EPR spectroscopy under static and pulsed electric fields (Fig. 1). These allow some empirical correlations between spin Hamiltonian parameters, molecular orientation, and the strength of the magnetolectric coupling.



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## Powder and single crystal CW and Pulse EPR Studies of Alkene Adsorption over Cu<sub>2.931</sub>Zn<sub>0.069</sub>(btc)<sub>2</sub>

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The porous coordination polymer HKUST-1 (Cu<sub>3</sub>(btc)<sub>2</sub> (btc = 1,3,5-benzenetricarboxylate)) is one of the most studied metal-organic framework (MOF) compounds. Due to its high pore volume and coordinative unsaturated (cus) cupric ion sites HKUST-1 is particularly interesting for gas adsorption and separation. At the same time, through its ability to replace zinc atoms by paramagnetic Cu<sup>2+</sup> ions, HKUST-1 offers the opportunity to explore adsorption phenomena on a local microscopic scale by electron paramagnetic resonance (EPR) spectroscopy. In the present work we studied the interaction of alkene molecules with the cus Cu<sup>2+</sup> sites in zinc-substituted Cu<sub>2.931</sub>Zn<sub>0.069</sub>(btc)<sub>2</sub> using continuous wave (cw) and pulsed EPR.

As ethylene adsorption shows, for example, the coordination geometry of the cupric ions in the Cu/Zn paddlewheels changed from square planar to square pyramidal due to interacting with π-bond of the adsorbate. However, for a detailed characterization of the structure of adsorption complexes it is necessary to have knowledge about the orientation of magnetic tensors. This information can be obtained from angular dependent cw EPR measurements of small MOF single crystals using dielectric resonators.<sup>1</sup>

In addition, the interaction between the gas molecules and the cupric ions was investigated by pulsed EPR methods that provide the <sup>1</sup>H hyperfine coupling parameters of adsorbed molecules. Based on these parameters and supporting DFT computations we suggest structural models for alkenes adsorption complexes formed at the Cu<sup>2+</sup> ions in HKUST-1.

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## Precise determination of the direction of the transition dipole moment by the study of the magnetophotoselection effects in triplet states

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Magnetophotoselection (MPS) can be observed in time-resolved electron paramagnetic resonance (TR-EPR) spectra of triplet states of dye molecules produced by photoexcitation. It manifests as a relative intensity change of the principal features of the spectra when passing from isotropic to polarized excitation light, or when the polarization direction of the light is varied, which are common situations when working with frozen solutions of the dye molecules, and using laser excitation.

In the past, MPS was used in a simple way in molecules of sufficient symmetry to determine the alignment of the transition dipole moment (TDM) along one particular symmetry axis of the electron distribution.<sup>1</sup>

We show that magnetophotoselection can be exploited to determine with a good precision the 3D orientation of the TDM in the molecule.

The method makes use of the change in the lineshapes of the TR-EPR spectra upon use of differently polarized laser light to excite an optically clear glassified solution of a dye at low temperature. The simulation of the spectra required extension to the standard simulation programs, with the introduction of the calculation of the distributional orientation of the excited molecules as a function of the light polarization direction. A global fitting of the lineshape of the spectra allows the determination of the orientation of the TDM in the zero-field splitting (ZFS) reference frame.<sup>2</sup>

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## Simultaneously Coupled 4 in 1 Operando EPR/XAS/ATR-IR/UV-vis Spectroscopy for Monitoring Catalysts at Work

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In this work, the first 4 in 1 simultaneously coupled EPR, XANES/EXAFS, ATR-IR and UV-vis spectroscopy has been developed for monitoring gas-liquid phase catalytic reactions. As a model reaction, the selective aerobic benzyl alcohol (BnOH) oxidation to benzaldehyde (BA) over a Cu<sup>I</sup>OTf/TEMPO catalyst system has been chosen to unravel Cu/TEMPO intermediates and active species which had been controversially discussed in literature.<sup>1</sup> EPR provides detailed information on the time-dependent redox behavior of paramagnetic Cu<sup>II</sup> (d<sup>9</sup>, S = ½) and TEMPO (S = ½) species in the reaction solution. While XANES/EXAFS and UV-vis spectroscopy are able to reflect all valence and nucleation states of Cu, yet in less detail, due to their spectral superposition (Fig. 1). Therefore, Multivariate Curve Resolution with Alternating Least Squares Fitting (MCR-ALS) was used. The real time conversion of BnOH to BA was followed by ATR. The results indicate that an initially formed tetracoordinated (bpy)(NMI)Cu<sup>I</sup> complex is converted to an EPR-active (bpy)(NMI)Cu<sup>II</sup>OOH monomer and an EPR-silent dinuclear [(bpy)(NMI)Cu<sup>II</sup>μ-OH]<sub>2</sub> which is irreversibly cleaved during the course of the reaction into EPR-silent (bpy)(NMI)(OOH)Cu<sup>II</sup>-TEMPO. Both Cu<sup>II</sup> monomer and dimer are catalytically active in the initial step of the reaction. We found that gradual formation of non-reducible Cu<sup>II</sup> leads to slight deactivation of the catalyst. Based on these results a new reaction mechanism is proposed.

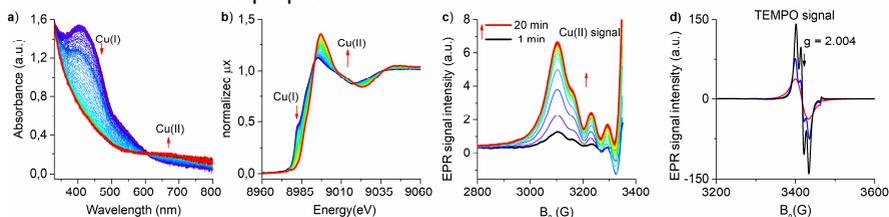


Figure 1. Changing with time of a) UV-vis, b) XANES, c) EPR spectra of 25 mM Cu<sup>I</sup>OTf, 1 equiv. bpy, 2 equiv. NMI and 1 equiv. TEMPO in CH<sub>3</sub>CN upon bubbling of O<sub>2</sub>; d) EPR spectrum of TEMPO under Ar before and after bubbling of O<sub>2</sub> for 20 min ((black line and red lines, respectively) and after addition of BzOH to the above Cu solution (blue line).

The new coupling technique is not only limited for monitoring gas-liquid phase reactions but also for heterogeneous catalytic processes under flowing gases at elevated temperature.

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## EPR spectroscopy provides insights into Cr/PNP based ethylene tetramerisation catalysis

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Ethylene oligomerisation is an important commercial route to 1-hexene and 1-octene, precursors for surfactants and co-monomers for polyethylene.<sup>1</sup> Increasing demand for 1-octene has fuelled research into selective tetramerisation. The industrial process involves highly active Cr/PNP (PNP = (R<sup>2</sup>)<sub>2</sub>PN(R<sup>1</sup>)P(R<sup>2</sup>)<sub>2</sub>) based catalyst systems and is up to 70% selective for 1-octene. However, the catalytically active species and the underpinning mechanism are still unclear.<sup>1,2</sup> The active catalyst is formed by activating Cr<sup>I</sup> or Cr<sup>III</sup> precursors with alkylaluminium in presence of a PNP ligand and a weakly coordinating anion such as (Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>)<sup>-</sup>. The Cr/PNP complexes formed can undergo ligand redistribution, reduction and disproportionation, resulting in the formation of various species with different oxidation states and altered total electron spin.

Paramagnetic species from discrete catalyst precursors to ongoing catalysis were examined *in situ* by continuous wave EPR spectroscopy. In the context of catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. To this end, relaxation filter-based pulse EPR methods were employed on a mixture of discrete Cr<sup>I</sup> and Cr<sup>III</sup> precursors with different spin states to demonstrate recovery of the individual component spectra.<sup>3</sup> This is demonstrated on activated Cr precatalysts for unravelling the various species formed. To obtain additional structural information on these intermediates pulse EPR experiments such as transient nutation for assessing spin states and hyperfine spectroscopy have been applied in combination with a quantum chemistry approach.

The use of selectively isotope labelled substrates and catalyst precursors in EPR time course experiments has provided unequivocal evidence for the transient formation of a bis-ethylene chromium species that has been postulated early in the catalytic cycle but eluded structural characterisation. Here we will present its EPR-derived structure and present insights into the mechanism of its formation derived from quantum chemistry.

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## Identification of reactive radical intermediates in photocatalytic systems by indirect EPR techniques

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Metal oxide based photocatalysis represents a widely studied topic due to its promising applications as well as several yet not fully understood issues of the structural, surface and bulk properties of the photocatalytic materials and the structure-activity relationship in combination with the various kinds of doping and modification of the photocatalysts<sup>1-3</sup>. EPR study of the primary electron transfer processes in the powdered photocatalysts at low temperatures combined with the detection of reactive radical species in dispersed systems brings a valuable contribution to the unraveling of these open questions and represents an important tool by the evaluation of the photoinduced activity of the new photocatalytic nanomaterials. Although EPR provides a direct detection of free radicals, in the photochemical investigations we are often forced to use indirect techniques to observe the generation of non-persistent paramagnetic species. A well established EPR spin trapping approach is based on the addition of unstable radical intermediates to diamagnetic nitron or nitroso compounds (spin traps) forming relatively stable nitroxide spin-adducts detectable by cw-EPR<sup>4</sup>. While the absence of a spin-adduct EPR signal does not necessarily mean that radical species are not present in the investigated system, the observation of a spin-adduct signal does not automatically imply the occurrence of the direct trapping process. The formation of spin-adducts may reflect not only the genuine spin trapping, but also the alternative reaction pathways, which becomes even more relevant in the complex systems of irradiated photocatalysts. Nevertheless the careful choice of the spin trapping agent and the specific adjustment of the experimental conditions enable the monitoring and unambiguous identification of reactive radical intermediates, which can help us to gain a comprehensive picture on the photoinduced processes undergoing upon light exposure of the photocatalysts in suspensions.

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## Posters





## First-principles investigation of spin-phonon coupling in vanadium-based molecular spin qubits

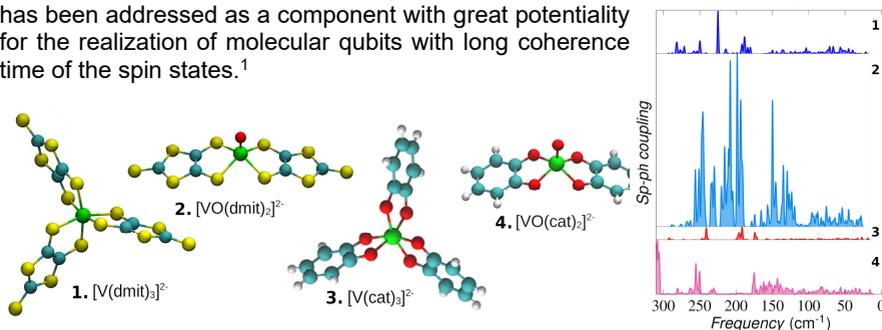
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Today, a steadily growing community of scientists is developing the tools of a new science that merges quantum physics and theoretical computer science, called quantum information science. Its basic constituent is the quantum analogue of the classical bit, say the qubit. In the development of spin-based quantum technologies it has become clear that molecules carrying a paramagnetic center represent particularly versatile building blocks as they can offer a high structural versatility. Synthetic chemistry can play a fundamental role in modulating specific interactions between microscopic constituents as phonons and spins in order to achieve the desired molecular properties. Among coordination compounds, the vanadyl moiety has been addressed as a component with great potentiality for the realization of molecular qubits with long coherence time of the spin states.<sup>1</sup>



One of the possible sources of relaxation of the spin state is represented by interaction of the spin with the lattice environment. The correlation between structure and spin-phonon coupling is complex in nature and first-principles calculations are the only way to quantitatively unveil it. The average magnitude of the spin-phonon coupling, here addressed by means of periodic-DFT and post Hartree-Fock calculations, has been found to correlate with experimentally accessible physical quantities as spin-lattice relaxation time  $T_1$  measured with different techniques such as magnetic resonance and AC susceptibility magnetometry, as a function of temperature. This suggests an easy and qualitative way to experimentally assess the potential of a magnetic molecule to function as a qubit.

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## Visible-light-responsive TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> composite photocatalyst – EPR spin trapping study

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One of the promising ways to improve the photocatalytic activity of semiconductor based photocatalysts and extend it towards visible light represents the combination of two semiconductors forming a suitable heterojunction. This may lead to an increased concentration of electron-hole pairs on the surface of the photocatalyst and suppressed recombination of the charge carriers. Heterojunction between two semiconductors, a visible-light-responsive (e.g.  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>) and a UV-light responsive with the optimal band positions to form reactive oxygen species (ROS) (e.g. TiO<sub>2</sub>) may lead to a promising composite with extended working region in the visible-light, while at the same time being able to decompose organic and inorganic pollutants. EPR spin trapping technique was used to study the ability of a series of TiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> composites with alternating amounts of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> (**B**) and TiO<sub>2</sub> (**T**) semiconductors to generate ROS upon photoexcitation. Spectra were measured *in situ* with the photocatalyst suspensions containing the spin trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO).

All the prepared composites (**TB**) have exhibited higher photocatalytic activity than commercially used benchmark TiO<sub>2</sub> (P25) when exposed to UV light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) in water suspensions. Pure  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> has displayed inferior photocatalytic activity due to its small specific surface area and fast recombination of the photogenerated charge carriers. An apparent beneficial effect of increasing amount of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> in the composite photocatalyst has been observed. Possible formation of the p–n heterojunction between two semiconductors may have led to an effective charge carrier separation of the photogenerated electrons and holes and to an overall improvement of the photocatalytic activity. Alongside the high UV light activity, these composite photocatalysts have shown a visible-light photocatalytic activity. When suspended in dimethylsulfoxide and irradiated by visible-light **TB** composites have shown quite a significant trend of correlation between the amounts of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and photocatalytic activity. Overall we observed a beneficial combination of two semiconductors obtaining a promising photocatalyst with outstanding UV light and apparent visible-light responses, which predetermines its usage in solar-light induced photocatalytic processes.

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## E S R and PALS characterization of bulk vs. confined organics in inorganic matrices

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The bulk vs. confinement problem represents one of the actual and hot topics in the condensed and soft matter physics. Most of the information about the potentially altered structural-dynamic state of confined *organic compounds (fillers)* in various confining *inorganic matrices (confiners)* are obtained by **classic experimental techniques**, such as structural (e.g. **XD**), thermodynamic (e.g. **DSC**) and dynamic (e.g. **BDS, NS**) ones.<sup>1,2</sup> At present, it is generally accepted that the overall confinement effect appears to be a result of the complex mutual interplay of the following two main factors: i) geometric restriction of the pores on the *medium* in a given *matrix* and ii) the mutual interaction of the *medium's* particles with the pore surface wall of the *matrix*. On the other hand, **non-traditional techniques** based on various extrinsic *probes*, such as *spin probes* in **ESR**<sup>3</sup> or *ortho-positronium probe* in positron annihilation lifetime spectroscopy (**PALS**)<sup>4</sup> are essentially less extended, although they can provide, in principle, more microscopic insights into the changed structural-dynamic situation of a given *organic medium* in the *inorganic matrix*. In contrast to the classic techniques, **ESR** and **PALS** concern the three-component character of the confined *organics-inorganics-extrinsic probe system*.

In our contribution we present a current overview of the results of systematic **ESR** investigations on structurally different *model organic media* confined in *inorganic matrices*. The former include non-polar *media* such as *n-undecane*<sup>5</sup>, *n-hexadecane*<sup>6</sup> and *n-propanol*<sup>7</sup> as a representative of class of protic polar *fillers* and the latter a series of various *silica-based matrices* of different pore size, pore morphology, i.e., pore size distribution and mutual pore interconnectivity as well as of pore surface composition. The observed spectral features and trends are discussed in terms of the mutual interaction of polar *spin probe TEMPO* with apolar vs. polar *medium* and non-polar vs. polar, irregular and regular, virgin and silanized *silica-based matrices* as well as of its reorientation mobility; the latter is related to the structural-dynamic changes through free volume redistribution in the bulk vs. confined *media* as detected by **PALS technique**.

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## Spin-orbit coupling and zero-field splitting in high-spin centers in solids

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High-spin ( $S > 1$ ) defects and impurities in extended periodic systems attract tremendous attention as promising tools in quantum sensing and quantum information processing. However, in many cases, their electronic structure and microscopic configuration cannot be deduced from the experimental EPR data alone. Therefore, state-of-the-art first-principles calculations are necessary to obtain a complete EPR fingerprint of a high-spin center.

Accurate prediction of EPR parameters often requires the inclusion of a spin-orbit coupling and, therefore, effective relativistic treatment. In addition, it is advantageous to consider solid-state paramagnetic centers within the supercell approach, which is commonly used in materials science and is devoid of spurious effects of finite size. Here we present our recent progress in EPR calculations for solid-state high-spin centers based on the plane-wave density functional theory (DFT) including the spin-orbit coupling.<sup>1</sup> We will focus especially on the zero field splitting (ZFS), which has been the least developed parameter in computational solid-state EPR.<sup>2</sup> Finally, we apply the presented formalism to a few high-spin defects in semiconducting host materials.

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## Dissolution DNP without Solution

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Dynamic nuclear polarization (DNP) for the enhancement of the NMR signals of specific metabolites has recently found applications in the context of magnetic resonance imaging (MRI). Currently, DNP signal enhancement is implemented in clinical systems through the use of exogenous stable organic free radicals, known as polarization agents (PAs), mixed in a solution with the metabolite of interest. These PAs are medically undesirable and thus must be filtered out prior to patient injection - a task that involves considerable technical complexity and consumes valuable time during which the polarization decays. Here, we aim to demonstrate DNP enhancements large enough for clinical relevance using a process free of exogenous PAs and without dissolving the metabolite of interest. This is achieved by processing (soft grinding) the metabolite in its solid form and subsequently exposing it to plasma in a dilute atmosphere to produce chemically-unstable free radicals (herein referred to as electrical-discharge-induced radicals - EDIRs) within the powder. These samples are then subjected to the normal DNP procedure of microwave irradiation while placed under a high static magnetic field, and their NMR signal is measured to quantify the enhancement of the protons' signal in the solid. Proton signal enhancements (measured as the ratio of the NMR signal with microwave irradiation to the NMR signal without microwave irradiation) of up to 150 are demonstrated in glucose.<sup>1</sup> Furthermore, in subsequent experiments, carbon polarization of ~ 4.5% is also achieved. Upon fast dissolution, the free radicals are annihilated, leaving the sample in its original chemical composition (which is safe for clinical use) without any need for filtration and cumbersome quality control procedures. We thus conclude that EDIRs are found to be highly efficient in providing DNP enhancement levels that are on par with those achieved with the exogenous PAs, while being safe for clinical use. This opens up the possibility of applying our method to clinical scenarios with minimal risks and lower costs per procedure.

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## Optically-induced Dynamical Nuclear Polarization in diamond

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Magnetic Resonance Imaging (MRI) is a widely used technique for medical diagnostic, and as a tool for life sciences in general. Though it enables to perform high contrast imaging, certain applications, such as <sup>13</sup>C MRI for imaging of metabolic/enzymatic conversion processes, which would be useful for cancer detection, suffer from a low sensitivity. In the recent years, various techniques have been explored in order to improve the sensitivity, most often one aims at enhancing the nuclear spin polarization above the thermal value. One of these techniques, called Dynamical Nuclear Polarization (DNP), relies on the transfer of polarization from electron spin to the nuclei.<sup>1</sup> Diamond is a promising material for DNP, since higher polarization values can theoretically be reached by first shining light on the negatively charged Nitrogen Vacancy defect (NV<sup>-</sup>), and then transferring its polarization to the surrounding <sup>13</sup>C nuclei, through the use of microwave irradiation.<sup>2,3</sup>

We present results concerning the hyperpolarization of <sup>13</sup>C in bulk diamond crystals, as well as the characterization of Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR) properties of powders (particle size in the 10nm - 10 μm range). In NMR, we measured the nuclear  $T_1$  time of such powders with either natural abundance of <sup>13</sup>C or, up to 30% enriched in the <sup>13</sup>C isotope. The enhancement of NV<sup>-</sup> polarization under laser illumination, which is a prerequisite for hyperpolarization, has been observed in pulsed EPR. However, detecting the hyperpolarized signal of diamond powder (in the above-mentioned size range) present different challenges, that we will review. As a proof of concept for future imaging experiments, we report the hyperpolarization of a diamond single crystal and its observation in a high-field 11.7 T preclinical MR system.

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## Photoinitiating system based on a well-defined titanium complex – an EPR study

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A newly-synthesized quinoline-derived titanium complex (**TiQ**) demonstrates photosensitizing properties when treated with an iodonium salt (Iod) to initiate, under visible light irradiation, the free-radical photopolymerization of acrylate monomer in aerated/laminated conditions, the cationic photopolymerization of epoxy monomer under air, along with the *in situ* formation of Ti-based nanoparticles inside coatings. The photochemical properties of the **TiQ**/Iod photoinitiating system were investigated by EPR, laser flash photolysis, and real-time Fourier transform infrared spectroscopy, providing an insight into the possible radical/cationic reaction pathways.<sup>1</sup> The generation of paramagnetic species caused by the photoexcitation of **TiQ** in de-aerated benzene was evidenced by *in situ* EPR spin trapping technique using nitrosodurene (ND) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin traps. The EPR spectra measured after LED@400 nm exposure of **TiQ**/Iod/ND evidence the trapping of 4-methylphenyl radical, produced by **TiQ**/Iod electron-transfer reaction and the homolytic cleavage of the carbon-iodine bond of Iod, forming a stable \*ND-(4-methylphenyl) spin-adduct. The photoexcitation of **TiQ**/Iod/benzene using LED@400 nm source in the presence of DMPO resulted in the immediate generation of six-line EPR spectrum characterized by the asymmetric signal intensities, reflecting so the occurrence of two DMPO spin-adducts of carbon-centered radicals with slightly different spin-Hamiltonian parameters, with the dominant signal attributed to \*DMPO-(4-methylphenyl) adduct. The EPR results clearly highlight that 4-methylphenyl radical is reactive toward acrylate double bonds and leads, in laminated conditions, to the free-radical photopolymerization of acrylate function with **TiQ**/Iod photoinitiating system.

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## Is time-reversal symmetry capable to deal with the EPR phenomena?

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The possibility of applying time-reversal (Kramers pairs) symmetry to the description of EPR shall be sketched. Herein, the time-reversal of a many electron system will be investigated with respect to the additivity ansatz of individual time reversal operators:<sup>1-4</sup>

$$\hat{K}_+ = \sum_j \hat{K}_j^A$$

The  $K_+$  operator relates the Kramers pairs via

$$\hat{K}_+ \psi_+ = \bar{\psi}_+ \quad \text{and} \quad \hat{K}_+ \bar{\psi}_+ = -\psi_+$$

The superB thing on  $K_+$  is that it's square defines an eigenequation with integer eigen numbers, i.e. quantum numbers:

$$\hat{K}_+^2 \psi_+ = -k^2 \psi_+$$

where,  $k = -N_0, -N_0+2, \dots, N_0-2, N_0$  with  $N_0$  being the number of unpaired electrons in the system (the  $-k^2$  degeneracy closely resembles Pascal's triangle). Hence,  $K_+^2$  introduces quantization of open shell systems as spin (S) does at the non-relativistic level of theory.

While,  $K_+^2$  commutes as with the non-relativistic so with the relativistic (Dirac-Coulomb) many electron Hamiltonian, spin does not commute with the relativistic (Dirac-Coulomb) Hamiltonian. Hence, one could conclude that  $K_+^2$  outperforms S. Hmmmm, but currently, this is actually not the case at all, because of the interpretive and predictive power of the spin Hamiltonian and /or the almost exclusive utilization of spin even in relativistic theories of the interaction between matter and magnetic field.

The perspective of  $K_+^2$  applicability with respect to interaction between matter and magnetic field shall be further discussed in this contribution, albeit currently even the author is rather pessimistic (yet there are three months till the conference, did I already mentioned that I am being pessimistic?).

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## Conformation of an individual polymer chain within a polymer nanoparticle

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The shape and size of nanoparticles crucially influences their optical and electric properties. Anisotropic nanoparticles can be used for a multitude of applications, including light emitting diodes (LED), photovoltaics and chemical sensors. However, it is challenging, to obtain anisotropic nanoparticles directly from polymerization. Many processes involve post-polymerization shaping of spherical particles. Recently, a heterophase polymerization, yielding ellipsoidal nanoparticles of Poly(9,9-dioctylfluorene) (**PF8**, see Fig. 1A) was published by Ruiz Perez *et al.*<sup>1</sup>. Conjugated polymer nanoparticles made from **PF8** are of interest, due to their different morphological phases and their electro- and photoluminescent properties. To understand the mechanisms behind the formation of these anisotropic nanoparticles, we carried out pulsed EPR experiments. **PF8** oligomers (n=1-6) with terminal TEMPO spin labels were synthesized. In this work, we used Double-Electron-Electron-Resonance (DEER, also known as PELDOR) to study possible changes in conformation and flexibility. The distance constraints have been modelled under the assumption of a worm-like-chain model. Additionally, a terminally labelled oligomer mixture was synthesized by Suzuki-Miyaura coupling polymerization (SMCP). We could describe the distance constraints by a Poisson distribution with the individual fractions of the worm-like-chain distributions of the corresponding oligomers (Fig. 1B). Nanoparticles with spin labelled oligomers were prepared and we determined the individual quantities of the oligomer fractions. We observe undisturbed flexibility and conformations of oligomers build into nanoparticles.

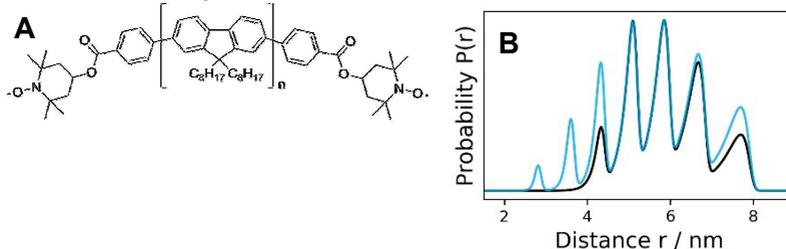


Figure 1. (A) Chemical structure of Poly(9,9-dioctylfluorene) (PF8) and (B) obtained distance distribution of SMCP polymerization (black) with fit of Poisson distribution (blue).

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## Application of EPR methodology towards catalysis

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Current research focuses on the development of sustainable chemistry involving industrial synthesis of chemicals and polymers with high market value and majority of these reactions are based on transition metal catalysts. Despite tremendous advances in the field of catalysis, the challenge of matching high activity and selectivity of precious metal catalysts with cheaper and potentially less toxic earth-abundant metals persists. In order to develop improved catalyst systems, understanding of already existing ones is crucial. These reactions often involve transition metal catalysts undergoing redox changes and/or formation of radicals during on-going catalysis giving rise to paramagnetic intermediates. Electron paramagnetic resonance (EPR) spectroscopy is extremely sensitive to these paramagnets and is an excellent tool to monitor the changes in their oxidation states as well as their surrounding ligand environment.

In the context of catalysis, we intend to use EPR spectroscopy for mechanistic understanding and the usefulness of this approach will be demonstrated on various catalytic systems. One example involving different paramagnetic oxidation states is chromium-based ethylene tetramerization.<sup>1, 2</sup> The presence of multiple species often complicates analysis due to their overlapping spectra. To this end, relaxation filter based pulse EPR methods were employed on a binary mixtures to demonstrate recovery of their individual spectra.<sup>3</sup> The full armoury of EPR techniques applied to an activated catalyst mixture provides the first unequivocal evidence for a bis-ethylene Cr<sup>I</sup> species that has previously been a proposed intermediate in the industrial process but has so far been elusive. In addition to Cr/PNP based ethylene tetramerization catalysis, application of EPR spectroscopy towards other catalytic reactions such as iridium based photoexcited reactions, copper based cross coupling reactions<sup>4</sup> etc. will be illustrated.

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## The Study of Crystal-field Anisotropy in Co(II)-based Single-ion Magnets

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In mononuclear Co(II)-based complexes with an easy-plane anisotropy a slow spin-lattice relaxation typical for single-molecule magnets (SMM) is observed in a non-zero magnetic field. The spin-lattice relaxation is mediated by the combination of direct and Raman relaxation processes, not the Orbach process as in conventional SMMs. The existence of low-energy intramolecular vibrations<sup>1</sup> allows the observation of a direct relaxation process within the ground Kramers doublet often induced by hyperfine interaction<sup>2</sup>. A correct estimation of crystal-field parameters and resulting energy barrier is of great importance for understanding of the spin-lattice relaxation in such anisotropic complexes. We have studied low-temperature X-band electron-paramagnetic resonance (EPR) of a series of Co(II)-based mononuclear compounds [Co(phen)<sub>2</sub>(dca)<sub>2</sub>], [Co(phen)<sub>3</sub>](tcm)<sub>2</sub>, and [Co(dcnm)(H<sub>2</sub>O)(phen)<sub>2</sub>](dcnm), where phen = 1,10-phenanthroline, dca = dicyanamide, tcm = tricyanomethanide, and dcnm = dicyanonitrosomethanide, with an easy-plane anisotropy. The relation between effective *g*-factors of the ground Kramers doublet estimated from EPR and spin-Hamiltonian parameters revealed strong rhombic anisotropy in all studied complexes with an energy barrier of at least 230 K. The experimental results were confirmed by *ab initio* calculations using SA-CASSCF/NEVPT2 method as implemented in ORCA package.

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## Spectroelectrochemistry of organoruthenium(II)– and organoosmium(II) – copper(II) complexes as potential anticancer drugs

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Conjugation of M(arene) fragments with another metal-based building block may result in an improved cancer selectivity and cytotoxicity. Mononuclear Ru(arene) and Os(arene) complexes demonstrated marked anticancer properties, and their use in vivo was characterized by low toxicity and good aqueous solubility. In addition, copper(II) complexes are well-known for their marked anticancer properties, related to the ability of a Cu atom to cycle between Cu(II) and Cu(I) oxidation states, leading to the production of reactive oxygen species (ROS), which are deadly for cancer cells. The novel homonuclear Cu(II) and heterodinuclear Cu(II)–Ru(II) and Cu(II)–Os(II) complexes with amidrazone scaffold and  $[\text{CuCl}_2]^-$  as a counterion were prepared and studied by cyclic voltammetry and spectroelectrochemistry<sup>1</sup>.

Complexes demonstrated quasi-reversible one-electron reduction of Cu(II) in complex cations and one-electron oxidation of  $[\text{Cu}^{\text{I}}\text{Cl}_2]^-$  counterion. The Cu-centered nature of redox events was further confirmed by UV–vis and EPR spectroelectrochemical measurements, where upon the first reduction step the paramagnetic Cu(II) state ( $d^9$ ,  $S = 1/2$ ) is converted into the EPR silent Cu(I) state ( $d^{10}$ ,  $S = 0$ ). In the region of the first one-electron oxidation step, a new EPR signal was observed, which is different from the EPR signal of the  $[\text{Cu}^{\text{II}}\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{-Cl}_2(\text{L}^{\text{H}})]^+$  cation and is characteristic for  $[\text{Cu}^{\text{II}}(\text{solv})_6]\text{Cl}_2$  species. Thus, the redox activity of the whole, bimetallic assembly is confined to the Cu sites, not involving the Ru(II)/Os(II) centers. The ability of investigated metal based amidrazone–morpholine hybrids to generate ROS in cell-free media was confirmed by spin trapping experiments by EPR spectroscopy. The addition of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap to DMSO/H<sub>2</sub>O solutions of studied complexes saturated with pure molecular oxygen led to the appearance of EPR signals characteristic of mainly oxygen centered spin adducts<sup>1</sup>.

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## Spectroelectrochemical study on electrochromic viologen systems

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The viologens are a well-known class of organic redox compounds used in such fields as electrochromic devices, herbicides, solar energy conversion and molecular electronics.<sup>1</sup> Polyelectrolyte-based electrochromic devices containing viologens provide well-defined colored states.<sup>2</sup> The electrochromic properties of the viologen systems can be modulated by varying the substituents at the nitrogen atoms. In this work, a series of the symmetric and asymmetric viologens in polyvinyl alcohol (PVA)-borax gel as an electrolyte was studied by spectroelectrochemistry. The simultaneous use of cyclic voltammetry, EPR and UV-vis-NIR spectroscopy enables unequivocal correlation between an observed coloration and the specific redox species involved. We have determined the dominant species at each stepwise varying potential and proposed the complete mechanism of the viologen reduction in polyelectrolyte.<sup>3</sup> It has been found that the dimer structures significantly contribute to the color observation under specified conditions. The differences in the spectroscopic features of the viologen radicals are discussed.

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## Copl, a periplasmic protein involved in copper resistance

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Copl is a novel periplasmic protein of 15 kDa, recently discovered while investigating the copper tolerance in the environmental bacterium *Rubrivivax gelatinosus*<sup>1</sup> and it is also present in pathogenic bacteria such as *Vibrio cholerae*<sup>2</sup>. It is naturally overexpressed when the bacteria are grown in the presence of a high copper concentration (up to 2 mM) and it can bind copper. The binding sites were studied by electron paramagnetic resonance in conjunction with various mutations. The purified protein binds two Cu(II) ions. One of the sites exhibits the characteristics of green copper cupredoxins, a still poorly described protein family.<sup>3</sup> The other site, partially emptied during the purification process, has a square planar geometry and parameters suggesting a 3 nitrogen 1 oxygen coordination. Mutations have been performed to localize the latter site within the protein. Possible roles for the metal ions will also be discussed.

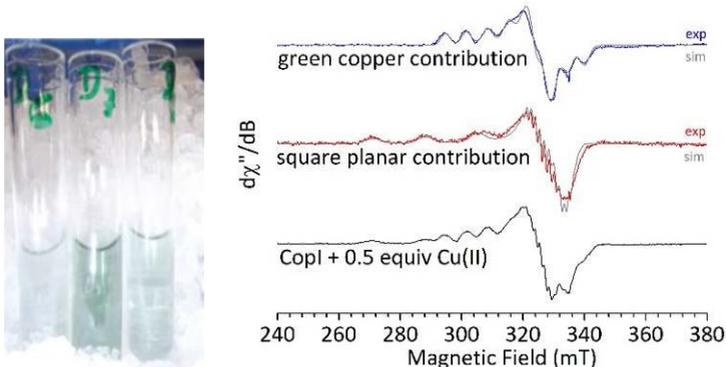


Figure 1. Left: purified soluble fractions containing Copl. Right: EPR spectrum of Copl complemented with Cu(II) and deconvolution into both contributions with their respective simulations.

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## Photoactivation of dispersed TiO<sub>2</sub>:g-C<sub>3</sub>N<sub>4</sub> nanocomposites studied by indirect cw-EPR techniques

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Indirect cw-EPR techniques, such spin-trapping or spin-scavenging, were successfully applied in the detection/identification of reactive paramagnetic species generated upon photoexcitation of the dispersed photocatalysts, bringing so the crucial information on their photocatalytic activities. Our contribution is oriented on the detailed study of photoinduced processes of composite photocatalysts prepared by mixing the chemically exfoliated graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and TiO<sub>2</sub> in various weight ratios *via* sonication in water and organic solvents. The generation of reactive oxygen species upon irradiation is strongly influenced by the position of valence (VB) and conduction band (CB) edges of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> as is shown in Figure 1. The results of EPR experiments are compatible with further photocatalytic studies confirming that the composites with the higher amount of titania are efficient in the systems where the hydroxyl radicals represent the main player responsible for the degradation of persistent organic compounds. On the other hand, photocatalysts with dominant g-C<sub>3</sub>N<sub>4</sub> content are effective in the systems, where the superoxide radical anions play a key role (e. g. decomposition of NO<sub>x</sub>).

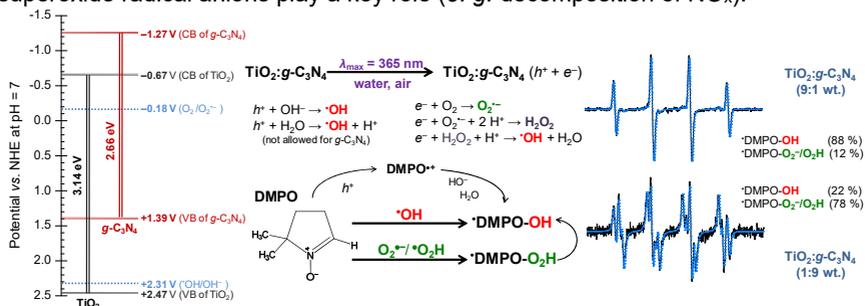


Figure 1. Alternative mechanisms of DMPO spin-adducts generation upon UVA exposure of TiO<sub>2</sub>:g-C<sub>3</sub>N<sub>4</sub> nanocomposites in water.

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## PELDOR on Trimeric Betaine Symporter BetP

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PELDOR (pulsed electron double resonance<sup>1</sup>) is a magnetic resonance method for distance, orientation, and dynamic measurements of two or more paramagnetic centers in macromolecules like proteins, RNA, or DNA as well as polymers. Here we apply this method to analyze the different states of the trimeric betaine symporter BetP<sup>2,3</sup>. This symporter does activate at osmotic stress and transports betaine and sodium through the membrane. BetP cycles through several states during the transport. From the periplasmic open via an occluded to a cytoplasmic open state. By PELDOR and site-directed spin labeling we probe the changes at different conditions as well as the occurring of different states.

We carried out molecular simulations of structures of the BetP monomer to interpret the PELDOR data, using the enhanced-sampling methodology EBMetaD<sup>4</sup>, whereby the dynamics of the protein are minimally biased to reproduce the experimental data. We illustrate how integrative simulations can aid interpretation of ambiguous structural and spectroscopic data on the BetP membrane protein.

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## EPR and DFT Studies of a Redox Non-Innocent Ligand Supported Vanadium Catalyst for Chemoselective Reduction of C=X (X = O, N) Functionalities

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Vanadium catalysis is the second largest application for vanadium (V) after its use as an additive to improve steel production. Molecular complexes of V are particularly useful and efficient (pre)catalysts for various oxidation processes. In contrast, the use of V in homogeneous reductions are extremely sparse. In this work, we report the first examples of polar organic functionality reduction mediated by V. An open-shell V<sup>III</sup> complex that features a  $\pi$ -radical monoanionic 2,2':6',2''-terpyridine ligand (Rtpy<sup>•-</sup>)<sup>1-</sup> functionalized at the 4'-position (R = CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>) catalyzes mild and chemoselective hydroboration and hydrosilylation of diverse functionalized ketones, aldehydes, imines, esters and carboxamides with appreciable turnover numbers (TONs) of up to ~1000. The X-band (9.40 GHz) electron paramagnetic resonance (EPR) spectrum of the V<sup>III</sup> complex (toluene glass,  $T = 123$  K) showed signals consistent with the presence of a quartet state  $S = 3/2$ . Thus, the observed spectral features were well-fit considering a V<sup>III</sup> ( $d^2$ ,  $S_V = 1$ ) center that is ferromagnetically coupled to a (TMSCH<sub>2</sub>tpy<sup>•-</sup>)<sup>1-</sup> ligand radical. Unrestricted density functional theory (DFT) calculations were in agreement with the model used to fit the EPR data.

## Exploring the potential of RIDME experiments at Xband frequencies

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Relaxation-Induced Dipolar Modulation Enhancement (RIDME) experiments have demonstrated the capability of providing distance ( $r$ ) information between two paramagnetic centers. Like other dipolar spectroscopies, it detects magnetic dipolar interactions from which the distance distributions are obtained using its  $\sim 1/r^3$  dependence. One of the most popular of such techniques is the four-pulse DEER experiment which observes the oscillations on the echo intensity of one of the spins while flipping the other with a  $\pi$ -pulse at a different microwave frequency. The experimental setup for DEER has to include two microwave sources and a resonator able to accommodate strong pulses at both frequencies. The principle of RIDME is very similar, except for the inversion of the pumped spin occurs through relaxation, which confers unlimited inversion bandwidth. Additionally, RIDME is a single frequency experiment since only microwave pulses at the observer frequency are required and, therefore, amenable to a more basic experimental setup. These features have rapidly attracted interest to the technique, which has already demonstrated very good performance at Q- and W- band frequencies.

In this contribution we report on the capabilities, challenges and limitations of Ridme at 9.4 GHz. For implementation and testing of the experiment, we used rigid model Gd-PyMTA complexes (Gd-rulers) featuring different distances between metal ions in deuterated and protonated solutions. Optimization of the experimental parameters and different strategies for cancellation of ESEEM effects were tested and RIDME experiments were performed and analyzed to successfully retrieve the anticipated distance. Calibration of the overtone coefficients showed very similar values to the ones found for RIDME experiments at higher frequencies. The most restrictive limitation for protonated samples was the steep decay of the background. As expected, in deuterated solvents longer relaxation times and better background behavior was found, although cancellation of the ESEEM oscillations was challenging.

## Low-Temperature Structural Transition in Bilayers of Doubly-Unsaturated Lipids by Pulsed EPR of Spin Labels

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The sub-zero temperatures between 80 and 240 K are important for cryopreservation of biological tissues, which motivates investigations of structural properties and dynamical properties of biological systems at these temperatures. Pulsed EPR of spin labels is sensitive to restricted orientational motions (stochastic molecular librations) of the labeled molecules, which are known to be coupled to the matrix rigidity.<sup>1-3</sup> In this work, the dynamics of DPPC (saturated lipid), POPC (mono-unsaturated) and DOPC (doubly-unsaturated lipid) model membranes were studied by pulsed EPR applied to the embedded spin-labeled stearic acids (5-DSA). Temperature dependence of anisotropic relaxation rate  $\Delta W$ , which is determined by stochastic librations, demonstrates faster increase for POPC membrane then for DPPC one (Fig.1). This can be explained by the larger rigidity of DPPC membrane, as POPC contains unsaturated C=C bond allowing free volume formation.<sup>3</sup> DOPC lipid has two unsaturated bonds; however, its  $\Delta W$  temperature dependence demonstrates similar behavior as POPC one, up to about 120K. Above this temperature, the increase of  $\Delta W$  becomes slower with temperature and coincides with the temperature dependence for DPPC membrane above  $\sim 180$ K. This behavior of temperature dependence of  $\Delta W$  can be explained by structural transition in the temperature range of 120-180K, in which the terminal segments of DOPC tails pack together.

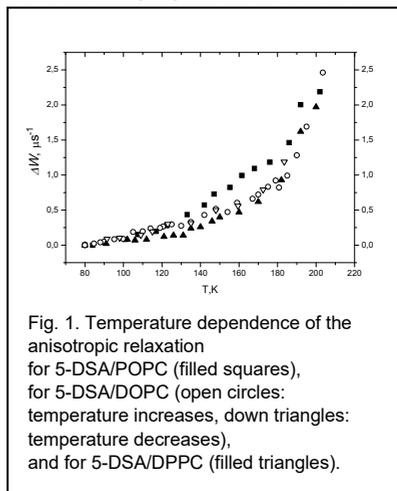


Fig. 1. Temperature dependence of the anisotropic relaxation for 5-DSA/POPC (filled squares), for 5-DSA/DOPC (open circles: temperature increases, down triangles: temperature decreases), and for 5-DSA/DPPC (filled triangles).

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## Combined EPR-DFT methodology to gain mechanistic insights in transition-metal catalysed oxidation reactions of organic molecules

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The oxidation of organic species by molecular oxygen, or autoxidation, is a spontaneous reaction, but it is very slow at room temperature, while high temperature processes are much faster but are unselective and usually result in combustion. The interest in catalysis for autoxidation reaction has grown steadily since the 1990s, following the emergence of green chemistry, but so far few man-made catalyst has been able to rival the efficiency and selectivity of enzymes.<sup>1</sup> Homogeneous catalysis protocols employing copper and iron have been known for a long time, however the mechanism of reaction is seldom investigated and generally poorly understood.<sup>2</sup> In the frame of the European Programme MSCA-Horizon 2020 "Paramagnetic Species in Catalysis Research (PARACAT)" we are working to develop a combined EPR-DFT methodology to gain mechanistic understanding of the transition-metal catalyzed benzylic oxygenation of (aryl)(heteroaryl)methanes. In previous works, some of us have shown that oxidation of these species employing molecular oxygen and copper(II)-based catalysts allows for good yields, however the knowledge of the reaction mechanism remains incomplete.<sup>3</sup> Our aim is to extend the reaction to Fe-based homogeneous catalysts and to employ advanced EPR techniques and DFT calculations to gain mechanistic understanding and allow for further studies concerning the role of the metal centre, ligand and solvent. First protocol outlines and spectroscopic results will be shown.

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## Determination of redox potentials of plant-type ferredoxin isoforms via EPR spectroscopy

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Ferredoxins (Fdxs) are soluble iron-sulfur proteins that function as electron acceptors and donors in diverse metabolic pathways in bacteria, algae, higher plants and animals. They are characterized by their acidity and low redox potentials (-230 to -420 mV). The unicellular green alga *Chlamydomonas reinhardtii* contains 12 different plant-type [2Fe2S]-Fdx isoforms.<sup>1</sup> The central and most abundant isoform Fdx1 has been first isolated and characterized extensively due to its essential role as electron acceptor of the photosynthetic transport chain. Under anaerobiosis and certain conditions of nutrient deprivation the [FeFe]-hydrogenase HydA1, which catalyzes the reversible reduction of protons to molecular hydrogen (H<sub>2</sub>), becomes another redox partner of Fdx1.<sup>2</sup> Since electron supply is one of the main limiting factors for commercial H<sub>2</sub> production applications, midpoint potentials of Fdx1 and other Fdx isoforms, which might function as electron donors of HydA, are of great interest.

The redox potentials of Fdx1, Fdx2 and Fdx5 have been detected via EPR, UV/Vis spectroscopic and electrochemical techniques previously.<sup>3</sup> However, the reported midpoint potentials are not identical. Here, we employed small volume EPR-based potentiometric titrations to identify midpoint potentials of selected Fdx isoforms from different organisms. In order to make a precise and certain detection, we made a detailed investigation of parameters that might affect the identified midpoint potentials. Buffer pH and identity, as well as the direction of the titration (oxidative or reductive) are changed in a controlled manner. The reduction potential we have determined for Fdx1 in a temperature independent buffer at pH 7.5 agrees very well with the only reported value that is also based on EPR-based potentiometric titrations.<sup>4</sup> The work presented here establishes a protocol for the accurate determination of redox potentials of FeS proteins via EPR, and also reports the midpoint potentials of several Fdx isoforms for the first time.

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## <sup>1</sup>H ENDOR spectroscopy at 9.4 T/263 GHz applied to the Y<sub>122</sub><sup>•</sup> radical in *E. Coli* Ribonucleotide Reductase

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Following the identification of the long-lived Y<sub>122</sub><sup>•</sup> radical in 1977, the ribonucleotide reductase (RNR) enzyme has become a paradigm for understanding the biological relevance of proton-coupled electron transfer (PCET).<sup>1</sup> Numerous subsequent EPR and ENDOR investigations of this intriguing radical have provided detailed information on its structure and orientation in the protein.<sup>2-6</sup> In a recent <sup>1</sup>H ENDOR study on Y<sub>122</sub><sup>•</sup> we demonstrated unprecedented orientation selection achieved at high magnetic field (9.4 T, corresponding to 263 GHz).<sup>7</sup> This allowed the resolution of previously obscured features in the <sup>1</sup>H ENDOR spectra, which were assigned to the C<sup>α</sup>-H proton of the tyrosyl group aided by DFT calculations.

Based on this work, we are presently developing a rigorous statistical treatment for the analysis of ENDOR spectra employing a spectral simulation routine developed in house. In this respect, the unambiguous determination of the number of coupled nuclei and automatic determination of their hyperfine coupling tensors are of principal interest. For this purpose, a Bayesian optimization procedure is envisioned as this can be combined with DFT-derived prior information. For the validation of this approach and the assignment mentioned above, respective ENDOR experiments on partially deuterated tyrosyl radicals in the RNR enzyme are currently underway.

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## ESR as a useful tool for titanocene hydrides study

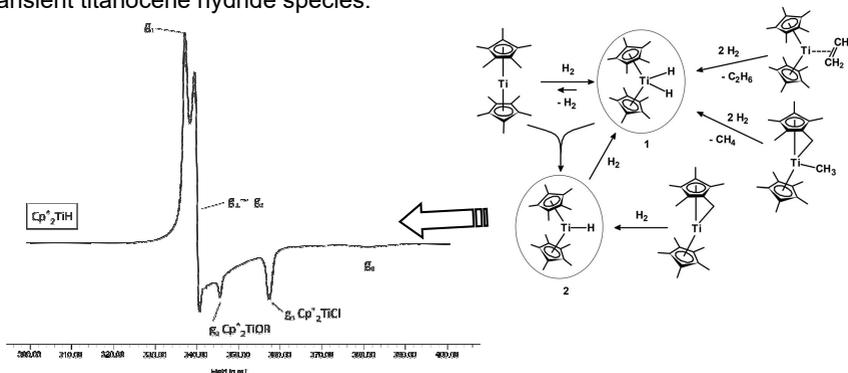
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Species like titanocene,  $[\text{Cp}_2\text{Ti}]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), or its hydride derivatives  $[\text{Cp}_2\text{TiH}_2]$  and  $[\text{Cp}_2\text{TiH}]$  could be considered to carry out the activation of molecular hydrogen. None of these compounds, however, has been identified through applying organometallic, metal or metal hydride reagents to the generally accessible titanocene dichloride. A recent improvement in the synthesis of decamethyltitanocene hydride  $[\text{Cp}^*\text{Ti}(\text{C}_5\text{Me}_4\text{CH}_2)]$ <sup>1</sup> brought us to investigate reactions with internal alkynes, conjugated butadiynes, as an authentic primary step in their catalytic hydrogenation. The reactivity of molecular hydrogen towards titanocene complexes differs depending on the steric congestion in the metallocene complexes and on their reducibility.<sup>2</sup>

This presentation will give an overview of ESR investigations of dihydrogen reactions carried out under mild conditions (22–70 °C, <1 bar) with a number of different titanocene complexes, with attention paid to the formation of transient titanocene hydride species.



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## Graphene-Based Hybrid Material with Quantum Bits Prepared by Double Langmuir–Schaefer Method

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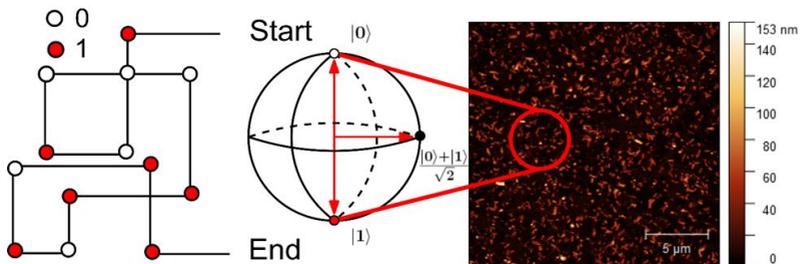
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The scalability and stability of molecular qubits deposited on surfaces is a crucial step for incorporating them into upcoming electronic devices. Herein, we report on the preparation and characterisation of a molecular quantum bit, copper(II)dibenzoylmethane -  $[\text{Cu}(\text{dbm})_2]$ , deposited by a modified Langmuir – Schaefer (LS) technique onto a graphene-based substrate. A double LS deposition was used for the preparation of a few-layer-graphene (FLG) on a Si/SiO<sub>2</sub> substrate with subsequent deposition of the molecules. Magnetic properties were probed by high-frequency electron spin resonance (HF-ESR) spectroscopy and found maintained after deposition. Additional spectroscopic and imaging techniques, such as Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were performed to characterise the deposited sample. Our approach demonstrated the possibility to utilise a controlled wet-chemistry protocol to prepare an array of potential quantum bits on a disordered graphene-based substrate. The deployed spectroscopic techniques showed unambiguously the robustness of our studied system with a potential to fabricate large-scale, intact, and stable quantum bits.

### Classical bits $\longrightarrow$ Quantum bits



## Host - Guest Interactions in Polymeric Gels Evidenced by EPR Spectroscopy

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EPR spectroscopy represents a suitable tool to investigate non-homogeneous systems using appropriate spin probes or spin-labelled constituents of a system that are sensitive to changes in their microenvironment.<sup>1</sup>

We investigated the influence of host-guest interactions between cyclodextrins and guest moieties covalently attached to polymeric structures that can build gel networks.

Three types of hydrogels have been studied, based on: a) a polymeric network resulted by reaction of isocyanate-functionalized polyethylene glycol with cyclodextrins, b) polyacrylate functionalized with cyclodextrin units and guest units for cyclodextrin and c) interpenetrated networks of polysaccharides functionalized with cyclodextrin and guest units. The guest units considered in this study were adamantyl and p-nitrophenyl moieties.<sup>2-4</sup>

The EPR spectra of spin-labelled gel networks indicated changes in dynamic of paramagnetic moieties as a result of functionalization with host and guest units. These changes have been correlated with rheological properties of gels.

Acknowledgement: This work was supported by PN-III-P4-ID-PCE-2016-0734.

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## TEMPO on graphene oxide for pollutants removal

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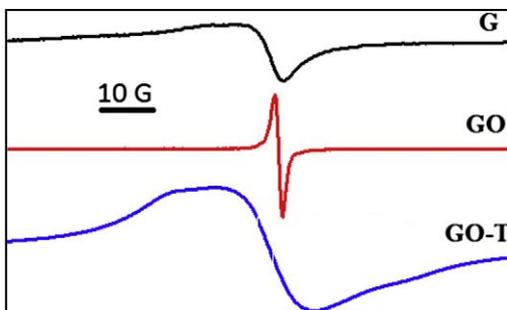
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Graphene oxide (GO) is a solid material based on exfoliated graphite (G) that contains, besides other oxygen-containing functionalities, carboxyl groups. These groups can be used to covalently link amines, like the amino-TEMPO stable free radical, yielding thus the material denoted GO-T. Besides, GO is known for its high capacity of absorbing a wide range of organic or inorganic pollutants.

The oxoammonium salt derived from the nitroxide free radicals is a strong oxidant that can oxidize a broad variety of organic pollutants from water. This very reactive salt is easily obtained by the oxidation of the nitroxide moiety with a wide range of co-oxidants, like sodium hypochlorite, bromine, strong acids, nitrogen dioxide, hydrogen peroxide, or even some enzymes.

The thus obtained GO-T material was firstly characterized by different methods (IR, Raman, thermal analysis, ESR, etc.) and then used as catalyst for removal of some test compounds that behave as pollutants (dyes, phenols, transition metal ions).



It was showed that the simultaneous presence of organic (methylene-blue) and inorganic (iron ions) pollutants affords the best results in a system that used GO-T as catalyst and hydrogen peroxide or sodium hypochlorite as final oxidant.

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## On the free radical scavenging activity of deprotonated forms of flavonoids and phenolic acids

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Tocopherols, flavonoids and phenolic acids are considered the most important groups of natural phenolic antioxidants. Experimental studies have shown that their free radical scavenging activity in aqueous solutions is significantly affected by pH.<sup>1,2</sup> Depending on the acidity of individual OH groups, flavonoids may be partially or fully deprotonated in the solution and formed anions positively affect their antioxidant action.<sup>1</sup> Due to the acidity of the COOH group, phenolic acids show similar behaviour.<sup>2</sup> Using EPR spectroscopy, it was confirmed that primary oxidation step of luteolin-7-O- $\beta$ -d-glucoside (cynaroside) takes place on the catechol unit leading to semiquinone radical anion.<sup>3</sup> Important role of the cynaroside deprotonated form in its redox and antioxidant behaviour was also pointed out. Therefore, for selected flavonoids and phenolic acids, we decided to perform DFT calculations of the antioxidant action thermodynamics in terms of hydrogen atom transfer (HAT) and the first step of sequential proton-loss electron-transfer (SPLET) in order to compare corresponding reaction enthalpies for non-dissociated and deprotonated species, i.e. phenoxide anions of flavonoids<sup>4,5</sup> and carboxylate anions of phenolic acids<sup>5</sup>. Found results confirm that in aqueous solutions, phenolic O–H bond dissociation enthalpies of deprotonated species are lower than in parent non-dissociated molecules. Although further deprotonation of an anion requires higher reaction enthalpy, differences usually do not exceed 10–15 kJ mol<sup>-1</sup>.

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## Triplet Fullerenes as Prospective Spin Labels for Nanoscale Distance Measurements by Pulsed Dipolar EPR

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Precise nanoscale distance measurements by pulsed EPR play crucial role in structural studies of biomolecules and their complexes. Nitroxide radicals are most common spin labels used in structural studies of proteins, nucleic acids and their complexes. However, the sensitivity of PELDOR on nitroxide labels is often insufficient, and distance measurements with label concentrations less than  $\sim 10^{-5}$  M are rarely feasible.

Herewith<sup>1</sup>, we have proposed the use of photoexcited fullerene as a new prospective spin label and, for the first time, demonstrated its applicability for PD EPR distance measurements in the nanometer range. The capabilities of new approach are demonstrated using covalently-bound fullerene-nitroxide and fullerene-triarylmethyl pairs, as well as supramolecular complex of fullerene with nitroxide-labeled protein. Stronger electron spin polarization and narrower spectrum of fullerenes compared to other triplets (e.g., porphyrins) boost the sensitivity, and superior relaxation properties allow PD EPR measurements up to a near-room temperature. Specifically, the pair of labels C60/TAM exhibits the most suitable properties for pulse dipolar EPR spectroscopy, such as high signal-to-noise ratio and high modulation depth. This allows distance measurements for systems with as low spin concentration as  $\sim 1$   $\mu$ M or less, even at X-band. Therefore, photoexcited fullerenes provide decent advancements, and in future, especially in combination with TAMs, they might allow obtaining way more exhaustive structural information on biological systems.

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## BODIPY-carbazole dyads studied by Time-Resolved EPR

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Time-Resolved Electron Paramagnetic Resonance (TR EPR) is broadly used to study the photoexcited triplet states and electron spin polarization mechanisms. Photoinduced dynamics in multicomponent systems of chromophores is often accompanied by strong electron spin polarization signals. The efficiency of the intersystem crossing (ISC) to form the long-lived excited triplet state is of paramount importance for applications of such systems. In particular, the spin-orbit charge transfer (SOCT) mechanism of ISC opens new possibilities for future development of triplet photosensitizers (TP). For instance, the compounds with this type of ISC show much lower dark toxicity with respect to TP bearing heavy atoms. Moreover, these purely organic compounds are very cost-effective.

In this work we used TR EPR to study the ISC processes in the new family of photosensitizers showing SOCT ISC – BODIPY-carbazole dyads. All measurements were done at 90 K using a homemade X-band TR EPR spectrometer based on Bruker EMX. BODIPY moiety was efficiently excited by 532 or 355 nm light. Interestingly, electron spin polarization pattern is drastically different depending on mutual arrangement of carbazole and BODIPY moieties. This clearly shows that charge separation precedes the formation of the long-lived triplet state and indicates the occurrence of the SOCT type ISC. The confirmation of this mechanism was achieved by direct analysis of triplet polarization patterns and further computer simulations of the spectra. Notably, no TR EPR signals were detected for the compounds with orthogonal geometry of two chromophores, whereas efficient ISC was found for non-orthogonal geometries. Finally, these dyads were successfully used as triplet photosensitizers for triplet-triplet-annihilation (TTA) upconversion and TTA-based delayed fluorescence. Thus, the application of TR EPR fruitfully complements optical spectroscopic studies of these promising systems.

## Dimerization of DNA G-quadruplexes: an EPR investigation

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G-quadruplexes are DNA secondary structures containing stacked guanine tetrads stabilized by central cations. They are formed by self-assembly of guanine-rich oligonucleotides by Hoogsteen base pairing. Studies have shown that G-quadruplexes form *in vivo* in oncogene regulatory regions and at telomeric ends of chromosomes, thus shortening cancer cell lifetimes<sup>1</sup>.

Many G-quadruplex species are known to form higher-order structures like dimers, which are believed to play a crucial role in G-quadruplexes biological activity. This makes the understanding of their structure and formation an important goal, where the EPR spectroscopy can make a substantial contribution. Recently, rigid Cu<sup>II</sup>-based spin labels were successfully incorporated into biomimetic tetramolecular DNA G-quadruplexes<sup>2</sup>. The potential of the DNA-bound metal spin labels for distance measurements was demonstrated by intramolecular pulsed EPR experiments on Cu<sup>II</sup> ions attached at 3' and 5' ends of G-quadruplex monomers<sup>3</sup>.

In the present work we use the orientation selective PELDOR (or DEER) and RIDME techniques to derive Cu<sup>II</sup>-Cu<sup>II</sup> distances in various forms of G-quadruplex dimers to gain insight into the topology of these higher-order structures. With the Cu<sup>II</sup>-based spin labels attached at either 3' or 5' ends of several G-quadruplex species, the dimerization at the opposite ends was studied.

EPR was also used to probe the dimerization of G-quadruplexes mediated by organic molecules. This provided information on both the resulting structures and the efficiency of the potential dimerization pathways. Interaction of G-quadruplexes with a variety of transition metal complexes makes EPR the method of choice for distance measurements within G-quadruplex-metal complex adducts, providing valuable information on binding modes.

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## Multi-frequency rapid-scan EPR at millimetre wave frequencies

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The development of the rapid scan technique was historically connected to the problem of the enhancement of the signal-to-noise ratio in NMR,<sup>1,2</sup> but it did not find wide application in NMR or EPR due to the rapid development of high power radio-frequency and microwave sources for pulse methods. However, the past decade is marked by the intense development of solid-state THz instruments, which has made it possible to perform EPR spectroscopy at very high frequencies and fields.<sup>3-5</sup> Unfortunately, the output power of such tunable THz sources is not sufficient for the implementation of pulse methods. Consequently, the rapid scan is the only affordable technique for multi-frequency investigation of spin dynamics at THz frequencies. To our best knowledge, this EPR technique was demonstrated at frequencies up to 94 GHz only.<sup>6</sup> Here we present results of the first successful implementation of multi-frequency rapid-scan EPR in the (sub)millimetre wave frequency range with access to extremely short relaxation times (several nanoseconds). The experiments were performed using a home built HFEPR spectrometer (University of Stuttgart) operated in induction mode.<sup>4</sup> The spectrometer does not require any resonator, and therefore, we are able to use frequency sweeps instead of magnetic field sweeps as it was done previously in the majority of experiments.<sup>7-9</sup> The main advantages of the frequency domain are the extremely high sweep rates (thousands of THz/s) and absence of eddy currents in the sample holder and/or resonator. The new HFEPR spectrometer in the Central European Institute of Technology (Brno) will further extend the frequency range and sensitivity of the rapid scan technique.

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## EPR Investigations of Cr Species in Olefin Polymerization Heterogeneous Catalysts

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In this poster we present an EPR investigation, aimed at elucidating the Cr oxidation and spin state in Cr based heterogeneous polymerization catalysts under different reaction and activation conditions. The Cr/SiO<sub>2</sub> Phillips catalyst is one of the World's most important industrial catalysts used in producing polyethylene since 1950s<sup>1</sup>. It is also among the most investigated and yet controversial catalytic systems as the nature of the active catalytic sites is still lively debated, in particular relative to the oxidation and spin states of Cr. This question is strictly connected to the initiation mechanism for ethylene polymerization at the Cr sites. Previous work have indicated that the nature of the Cr sites is largely dependent upon the activation and reaction conditions.<sup>2-5</sup> EPR spectra recorded at X and Q band frequencies indicate the presence of specific Cr(III) species formed upon reaction with ethylene starting from an oxidized Cr/SiO<sub>2</sub> catalyst.

Acknowledgement: Funding from the Marie Curie Action MSCA-ITN-PARACAT 813209 is gratefully acknowledged.

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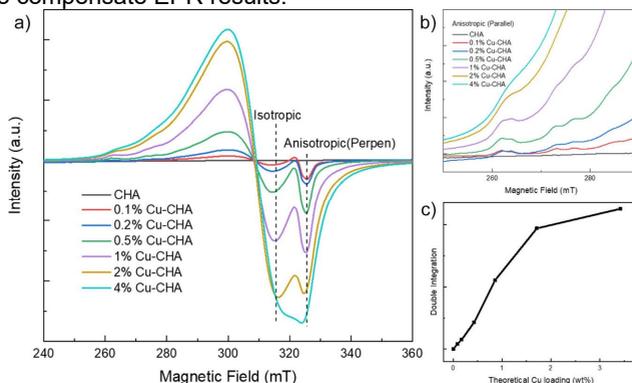
## Electron Paramagnetic Resonance (EPR) study of Cu-CHA Catalysts for Selective Catalytic Reduction (SCR) Reaction

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The efficient and thermal stable catalysts to eliminate major pollutant NO<sub>x</sub> in the exhaust gas of diesel engine have long been the pursue of scientists. Cu-chabazite zeolites system discovered in 2008 fulfilled almost all these requirements to use in the NH<sub>3</sub>-SCR reaction and has received intense study since then. In this research, electron paramagnetic resonance (EPR) is used as the major technique to characterize the Cu-CHA zeolites, which is also accompanied by other common techniques such as *in situ* FTIR spectroscopy, UV-Vis spectroscopy, H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD to compensate EPR results.



NO adsorption experiments monitored by *in situ* FTIR confirmed the existence of the dominant Cu<sup>2+</sup> species with trace amount of Cu<sup>+</sup> after oxygen activation. However, the oxygen residual from pretreatment interfere with the experiments and the spectra are dominated by various N<sub>x</sub>O<sub>y</sub><sup>n-</sup> species with raising baseline. EPR results also show significant difference between samples with low and high Cu loading. Whether this difference accounts for the different activity of samples with various loading under high and low temperature will be the focus of future study. EPR spectra of hydrated Cu-CHA samples confirmed the dispersion of Cu<sup>2+</sup> in most samples and the formation of Cu clusters in higher loading samples. Spin Hamilton parameters extracted from the simulation of EPR spectra are in good accordance with values in the literature<sup>1</sup>, and species after dehydration are identified to be Cu<sup>2+</sup> in the 6mr.

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## Characterization of High-Spin Complexes Relevant in molecular Magnetism by Frequency-Domain THz-EPR

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The magnetic behavior of single-molecule magnets (SMMs) below their characteristic blocking temperature, *i.e.* slow relaxation of field-induced magnetization, renders them potential candidates for spin-based nanoscopic data storage. For improving their magnetic anisotropy, precise determination of the zero-field splitting (ZFS) parameters  $D$  and  $E$  is crucial, since the energetic barrier for relaxation scales linearly with  $|D|$ . However, as the high-spin states of SMMs exhibit very large ZFS up to hundreds of  $\text{cm}^{-1}$ , their EPR transition energies exceed the frequency/field range covered by conventional single-frequency EPR spectrometers. Frequency-domain Fourier-transform (FD-FT) THz-EPR<sup>1</sup> employing broadband sources in the THz and FIR range allows probing a much wider range of transition energies. The FD-FT THz-EPR setup at BESSY II is highly versatile, enabling measurements from 5-370  $\text{cm}^{-1}$  by applying either coherent synchrotron radiation or using a Hg-arc lamp combined with external fields of 0-10 T and in various excitation geometries. We report on the recently implemented capability of our setup to measure very large EPR transition energies of several hundred wavenumbers, as featured by an increasing number of novel SMMs.

We have also explored the use of circular polarized THz radiation on compounds with large magnetic interactions as a means to determine their spin Hamiltonian parameters with even higher accuracy. A prototype study on the high-spin iron(III) ( $S = 5/2$ ) complex hemin is presented.

Furthermore, we have studied the magnetic properties and electronic structure of  $[\text{Fe}(\text{TPP})(\text{H}_2\text{O})_2]\text{ClO}_4$ , an iron(III) porphyrinoid compound, by FD-FT THz-EPR in combination with SQUID magnetometry, Mössbauer and theoretical calculations.<sup>2</sup> Its slow magnetic relaxation is rationalized by a spin-admixture model with a major contribution of the  $S = 5/2$  state ( $\approx 85\%$ ), leading to a strong ZFS with a large, positive axial anisotropy ( $D = +19.2 \text{ cm}^{-1}$ ).

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## CW and Pulse EPR Studies of nano-Liter Volume [FeFe]-Hydrogenase Single Crystals Using a Novel Self-Resonant micro-Helix

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To fully resolve the magnitudes and orientations of the g-, hyperfine, and quadrupole tensors of paramagnetic intermediates of an enzyme, the EPR investigation of single crystals is mandatory. Previous EPR studies on paramagnetic intermediates of a [NiFe]-hydrogenase active site using a 2 x 0.5 x 0.5 mm<sup>3</sup> (500 nL) single crystal were performed successfully in the past.<sup>1-2</sup> However, single-crystal experiments of other hydrogenases, such as the [FeFe]-hydrogenase, have not been possible so far due to significantly reduced crystal dimensions (1-30 nL). To study these limited sample volumes new technical advances had to be developed. Here we present a novel microwave resonant structure, the self-resonant micro-helix, for nano-liter samples that can be implemented in a commercial X-band (nominally 9.5 GHz) EPR spectrometer.

The self-resonant micro-helix (6.5 turns, inner diameter 400 μm, height 1.2 mm) provides a measured signal-to-noise improvement of a factor close to 30 (non-saturating samples) with respect to the best available commercial EPR resonators. A resonator efficiency of 3.2 mT/W<sup>1/2</sup> was experimentally determined, which corresponds to a 20 ns π/2-pulse at only 20 mW of incident power. The increase of EPR signal intensity, a resonator bandwidth of 90 MHz, and the very high resonator efficiency make the self-resonant micro-helix also advantageous for pulse hyperfine EPR experiments such as ESEEM and HYSCORE spectroscopies.

This advance in resonator design has allowed, for the first time, the collection of EPR data from a 0.3 x 0.1 x 0.1 mm<sup>3</sup> (3 nL) single crystal of [FeFe]-hydrogenase from *Clostridium pasteurianum* (Cpl; [6Fe]-cluster) in the H<sub>ox</sub> state and the determination of the g-tensor, Fig. 1. Additionally, HYSCORE spectra could be collected from the same protein single-crystal. Further applications of the new set-up will be discussed.

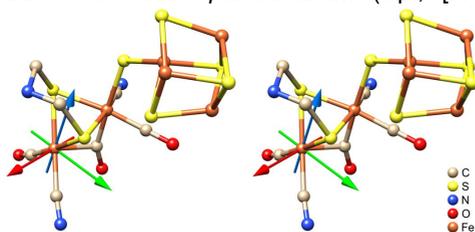


Figure 1. Stereo view of the proposed g-tensor of Cpl in the H<sub>ox</sub> state (g<sub>x</sub> red; g<sub>y</sub> green; g<sub>z</sub> blue).

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## EPR spectroelectrochemical study on 10-ethyl-7-oxo-7H,10H-pyrido[2,3-f]quinoxaline derivatives

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Quinoxaline derivatives exhibit group of compounds with interesting properties. Antiviral, antimicrobial, anti-tumor and anti-protozoan effects of several quinoxaline derivatives were reported<sup>1</sup>. Additionally, several quinoxalines possesses suitable properties in organic electronics<sup>2,3</sup>. However, some tricyclic quinoxalines exhibit carcinogenic activity<sup>4</sup>. Polyfunctionalized quinoxalines can be used in analytical chemistry as chromogenic chemosensor for selective ions determination<sup>5</sup>. Moreno et al. reported the effect of molecular structure on the reduction potential as well as on the antimicrobial activity of various quinoxalines. Higher antibacterial activity is observed at derivatives with less negative reduction potential<sup>6</sup>. Group of 10-ethyl-7-oxo-7H,10H-pyrido[2,3-f]quinoxaline derivatives with the substitutions at positions 2,3 and 8 was synthesized<sup>7</sup> and their spectral and photochemical properties were investigated<sup>8</sup>. Because the redox behaviour of N-heterocyclic compounds can significantly influence their potential biological activity, this study was focused on the electron transfer processes of studied derivatives and their investigation by cyclic voltammetry and EPR/UV-VIS-NIR spectroelectrochemistry<sup>9</sup>. In case of 10-ethyl-7H,10H-pyrido[2,3 f]quinoxalin-7-one and ethyl 10-ethyl-7-oxo-7H,10H-pyrido[2,3-f]quinoxaline-8-carboxylate derivatives, cathodic reduction represents a reversible one-electron process associated with the formation of corresponding radical anion. However in case of 10-ethyl-7-oxo-7H,10H-pyrido[2,3-f]quinoxaline-8-carboxylic acid derivatives, there are two independent cathodic steps. According to results from EPR/UV-VIS spectroelectrochemistry, the first irreversible process is associated with the reduction on pyridone ring and the second reversible step is the reduction on  $\pi$ -electron deficient pyrazine moiety besides formation of the corresponding anion radical.

Acknowledgement. We are grateful for the supports of the Slovak Grant Agency VEGA (contract 1/0466/18)

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## Multi-frequency electron magnetic resonance characterization of vanadium dopant sites in the metal-organic framework DUT-5(Al)

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Metal-Organic Frameworks (MOFs) are ordered porous crystalline materials constructed of metal ions connected by organic linkers, for which a diverse scale of applications are being explored (e.g. catalysis, gas adsorption, separation and storage). Two characteristic types of MOFs with one-dimensional pores are DUT-5(Al) ((Al<sup>III</sup>OH)BPDC, BPDC = biphenyl-4,4'-dicarboxylate)<sup>1</sup> and MIL-53(Al) ((Al<sup>III</sup>OH)BDC, BDC: 1,4-benzenedicarboxylate).<sup>2</sup> The framework of the latter structure exhibits breathing: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure. Recently we have shown that EPR spectroscopy using V(IV) as a paramagnetic probe can distinguish between these two states for V-doped MIL-53(Al).<sup>3</sup> Whereas breathing has not been reported for DUT-5(Al), it has been observed for COMOC-2(V) ((V<sup>IV</sup>=O)BPDC).<sup>4</sup> Measurements on V-doped DUT-5(Al) revealed an EPR spectral component that showed similar characteristics as V<sup>IV</sup>=O in large pore MIL-53(Al), but also other components were found.<sup>5</sup>

Here we further explore the EPR spectrum of V-doped DUT-5(Al). Spin-Hamiltonian parameters are derived from X- (9.5 GHz), Q- (34 GHz) and W-band (94 GHz) spectra. At low concentrations of V two components are observed in the EPR spectrum: a large pore component and a broad-line component. Starting from 9% of V, two additional spectral components are revealed: a narrow-line component of isolated vanadyl centers that is most probably linked with a narrow pore phase of DUT-5(Al) and a broad structureless line of the V-concentrated phase (V<sup>IV</sup>=O)BPDC. The relative contributions of these four components, estimated through spectrum simulations, are evaluated as a function of V-concentration. The Q-band ENDOR spectra reveal interactions with <sup>1</sup>H nuclei of the BPDC linker.

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## TEMPO/PROXYL-derived bis(amide) monomers and dimers. Theory vs. Experiment

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Nowadays TEMPO and/or PROXYL based derivatives attract considerable interest because of their potential applications in chemistry, biology and medicine.<sup>1</sup> Newly synthesized TEMPO bis(amide) and PROXYL bis(amide) compounds are studied both theoretically and experimentally *via* EPR and UV-vis spectroscopy. Bonding and interactions between the two monomer units is explored by means of energetics at the DFT level of theory and Bond Critical Points (BCP) analysis. A comparison of calculated and experimentally obtained EPR parameters (g- and A-tensors) as well as UV-vis spectra vs. TD-DFT calculations are presented.

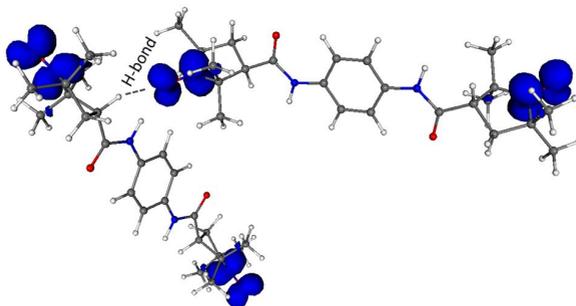


Figure 1: Structure of PROXYL bis(amide) dimer with hydrogen bond and spin density localization depicted

Acknowledgement: We are grateful to the Slovak Grant Agencies APVV (contract No. APVV-15-0079), VEGA (contracts No. 1/0598/16 and 1/0466/18) and SIVVP project( ITMS code 26230120002). DN is also grateful to Axa Inovátor 2019, a grant scheme to support students and young innovators.

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## Visualization of Relativistic effects on EPR Hyperfine Coupling Pathways

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Paramagnetic compounds represent an important class of technologically interesting materials. Paramagnetic NMR spectra contain a wealth of information but their interpretation is often challenging. Significant progress in relativistic and nonrelativistic quantum-chemical methods for calculations of pNMR shifts has brought new tools for interpretation of experimental results. One of the most intriguing questions in the analysis of pNMR shifts concerns the pathways of the contact and pseudocontact shifts that sheds light on the structure-property relations for paramagnetic compounds. We present a new tool for visualization of hyperfine coupling pathways.<sup>1</sup> The plotted 3D-function is the difference between the total electron densities when the magnetic moment of the nucleus of interest is parallel and antiparallel to the external magnetic field and as such is an observable from the physical point of view. In contrast to the widely used visualization of spin density, our new approach depicts only the part of the electron cloud of a molecule that is affected by the interaction of the unpaired electron(s) with the desired nucleus. In case of heavy element compounds the new approach allows one to visualize relativistic effects on the hyperfine coupling pathway.

Acknowledgement: This work received funding from the from the Slovak Research and Development Agency (grant APVV-15-0726).

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## **<sup>13</sup>C hyperfine coupling characterization of the flavin semiquinone by EPR techniques**

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Flavin ring is the active centre of a large family of proteins called flavoproteins. It includes enzymes, charge carriers or sensing proteins as LOV and BLUF. Together with the oxidized and reduced states, flavin into the protein can reach a semiquinone (paramagnetic) state that in many cases has functional relevance. Flavin ring in the semiquinone state had been extensively studied by cw, pulse and multiple resonance EPR techniques. In particular, the spin distribution within the flavin ring has been characterized by measuring the weak hyperfine couplings with nuclei of the molecule. The spin distribution has also been calculated from different theoretical methods.

Couplings with nitrogen nuclei and protons has been reported in many studies. On the other hand, EPR studies of flavins labelled with oxygen or carbon isotopes are scarce. In this contribution, we show our results of the characterization by EPR techniques of the model flavoprotein flavodoxin where the carbon nuclei at positions 2 and 4a of isoalloxazine has been enriched with <sup>13</sup>C (I=1/2) isotope. Combination of cw EPR, HYSCORE and ELDOR-detected-NMR techniques allows characterizing hyperfine couplings of these nuclei with the electronic spin of the flavin semiquinone. Comparison with calculated hyperfine couplings shows that the actual coupling is poorly estimated from calculations. This contrast with the case of nitrogen and proton couplings, where experimental and calculated results compare quite well. These results are discussed from a structural and mechanistic point of view.

## X- and Q-band EPR spectroscopy of HS Mn(II) complexes

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The EPR spectroscopy is a powerful technique for accurate determining the zero field splitting parameters of the high spin (HS) Mn(II) complexes, which characterize the axial and rhombic distortion of octahedral ion crystal field. The HS Mn(II) ion has an electronic configuration of 3d<sup>5</sup>, a ground state term of <sup>6</sup>S<sub>5/2</sub> and a spin quantum number, S = 5/2. The possible hyperfine interaction can be caused by isotope <sup>55</sup>Mn (100 % natural abundance and I = 5/2). The EPR spectra of HS Mn(II) ion recorded in the solid-state can be described by the following spin Hamiltonian:

$$H = \beta B g S + I A S + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + E(S_x^2 - S_y^2)$$

The first term describes the electronic Zeeman interaction, the second term represents the hyperfine interaction between unpaired electrons and the manganese nucleus, the last two terms define the zero field splitting interactions with D and E parameter representing the axial and rhombic part. The other symbols have their usual meaning. The first derivative, X-band ( $\approx 9.4$  GHz,  $h\nu_1 = 0.3$  cm<sup>-1</sup>) and Q-band ( $\approx 34$  GHz,  $h\nu_2 = 1.2$  cm<sup>-1</sup>) EPR spectra of powder Mn(II) complexes were recorded on EMX and EMX plus EPR spectrometers (Bruker BioSpin, Germany). The Mn(II) EPR spectra were measured at room temperature and 98 K. The EPR spectra were processed, evaluated and analyzed by the original Bruker software (WinEPR). The spin Hamiltonian parameter values obtained from the experimental EPR spectra were further refined by computer simulation. The powder EPR spectra of HS systems (S = 5/2) were computed by two original programs, „HighSpin“, (created by Ozarowski, 2014) and „VisualRhomb“, (created by Hagen, 2009). In the case of mononuclear Mn(II) complexes, the presence of HS Mn(II) spin state (S = 5/2) was revealed at both X- and Q-band frequencies. All the EPR spectra of mononuclear Mn(II) complexes were simulated on the basis of isolated high spin Mn(II) centers with g  $\approx 2.0$  and corresponding zero field splitting parameters, D and E. The zero field splitting parameter values obtained by computer simulation are typical of mononuclear HS Mn(II) complexes. The Q-band EPR spectrum of binuclear Mn(II) complex recorded at 98 K exhibited the multiplet with eleven well resolved resonance lines, which was due to Mn···Mn dipole-dipole interactions.

**Acknowledgement:** This work was supported by the Slovak Research and Development Agency under the contact No. APVV-15-0053 and by the Scientific Grant Agency of the Slovak Republic (Projects VEGA 1/0026/18 and VEGA 1/0686/17). We thank Ministry of Education, Science, Research and Sport of the Slovak Republic for funding within the scheme "Excellent research teams".

## Development of FTIR spectroscopy in high magnetic field

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We live in the digital era when the growing need for smaller and more energy efficient devices has made higher density data storage one of the most important technological quests. With dimensions close to a nanometer and the ability to store one bit of information, molecules called Single-Molecule Magnets (SMMs) give a possibility to move the data storage technology forward. For the investigation of SMMs, spectroscopic techniques, such as Electron Paramagnetic Resonance (EPR), are essential due to their ability to probe molecular and electronic properties directly. However, because of systems with large zero-field splitting, Fourier Transform Infrared (FTIR) spectroscopy in the high magnetic field is needed in order to access fundamental transitions in SMMs. We propose FTIR spectroscopy in high magnetic fields as a very important tool in the characterization of numerous materials, including SMMs. This method allows studying EPR of SMMs with very large zero-field splitting, mainly based on transition metal complexes<sup>1</sup> or lanthanides<sup>2</sup> that cannot be studied by common EPR systems since they do not provide experimental access to the magnetic resonance transitions. It also presents an ideal experimental technique that can probe band structure and elucidate electronic properties of novel 2D materials, such as graphene<sup>3</sup>. The method of FTIR spectroscopy in high magnetic fields will be mediated by compact FTIR magneto-spectroscopic setup built at CEITEC BUT. It consists of FTIR spectrometer coupled to the 16 Tesla cryogen-free superconductive magnet. The FTIR magneto-spectroscopic setup will allow us to perform a variety of magneto-optical measurements in infrared (IR) and terahertz (THz) spectral range.

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## EPR Study on Formation of Gold Nanoparticle in Solutions of Albumin and Hydrogels

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The interest in nanoparticle properties and interactions with relevant biological molecules or materials have attracted great interest due to their possible applications in the field of nanomedicine and nanotechnologies.

Here we present the results on monitoring the formation of gold nanoparticles in solutions of bovine serum albumin or in polysaccharide hydrogel matrices. Besides well-known methods used to characterize such systems (including electronic microscopy, rheology, DLS), in this study we involved electron paramagnetic resonance (EPR) spectroscopy. Both polysaccharide and Au species are diamagnetic, therefore we used spin-labelled polysaccharides or spin probes with affinity for gold nanoparticles. In this way it is possible to monitor different aspects: the formation of nanoparticles, the conformational changes of the protein or the changes in the gel networks.

Acknowledgement: this work was supported by PN-III-P4-ID-PCE-2016-0734.

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## Spin delocalisation in the radical cations of porphyrin molecular wires: a new perspective on EPR approaches

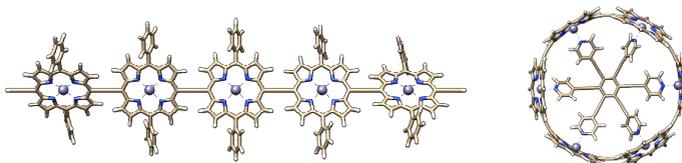
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The remarkable charge transport ability of naturally occurring porphyrins has incentivised synthetic organic chemists to consider artificial conjugated porphyrins as prime candidates for molecular wires in nano-scale electronic and spintronic devices. The intelligent design of truly viable molecular wires from porphyrin oligomers, however, requires an understanding of the fundamental structural parameters which dictate the extent of electronic communication. ESR spectroscopy has proven to be critical in elucidating the factors which determine the organic semiconductor behavior of porphyrins both in their photo-excited triplet states<sup>1</sup> as well as in their radical cation<sup>2</sup> and anion states.<sup>3</sup>

The study of the radical cations and anions of conjugated porphyrin oligomers has, until now, been reliant on analysing the linewidth of the ESR spectra. This analysis is based on the seminal work of Norris et al. who showed in 1971, using a newly derived equation, that the ESR signal of the primary light harvesting reaction in photosynthesis is consistent with an intermediate species involving a special pair of chlorophyll molecules.<sup>4</sup> Whilst the benchmark analysis of Norris can be a useful guide in most cases, it can also give rise to misleading conclusions regarding the extent of delocalisation. We show this to be the case in a novel series of *meso-meso* ethyne-linked linear and cyclic porphyrin oligomers (see below) using cw-ESR, pulse ENDOR, as well as supporting DFT calculations. According to these experimental and computational results, the deviations from the expected theoretical trend can be quantitatively justified by a non-uniformly distributed spin density.



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## Realization of Universal Quantum Gates with Spin/Qudits in Colloidal Quantum Dots

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Potential building blocks for multi-level *qubits* or *qudits* are intensively investigated because of the multi-dimensional Hilbert space ( $d > 2$ ) for encoding several bits per unit, reduced number of units and hardware size, and robustness against noise and error rates. These advantages over simple *qubits* could lead to novel scalable and downsized quantum computer architectures.

Although this type of *qudit* has been studied in transition metal (TM) ions and rare earth (RE) elements embedded in bulk solid state<sup>1</sup> and molecular systems,<sup>2</sup> its experimental implementation in universal quantum gates has not yet been achieved in quantum dots (QDs) doped with TM ions.<sup>3</sup>

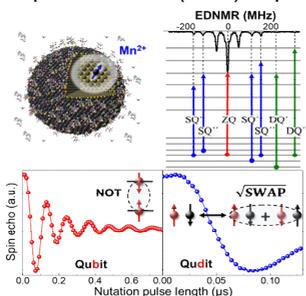


Figure 1. Top left. A single Mn ion confined in a QD creating a *qudit*. Top right. EDNMR spectrum and corresponding transitions. Bottom. Rabi oscillations implementing NOT and  $\sqrt{\text{SWAP}}$  quantum gates.

We demonstrate that hyperfine interactions in isolated Mn-ion confined in colloidal QDs (Figure 1) can be exploited to probe an arbitrary superposition of states between selected hyperfine energy level pairs by using electron double resonance detected nuclear magnetic resonance (EDNMR). This enables the observation of Rabi oscillations and the experimental realization of NOT and SWAP universal quantum gates that are robust against decoherence. We propose a protocol for cyclical preparation, manipulation and read-out of logic gates that could be implemented in QDs integrated in scalable quantum circuit architectures beyond solid state electron spin *qubits*.

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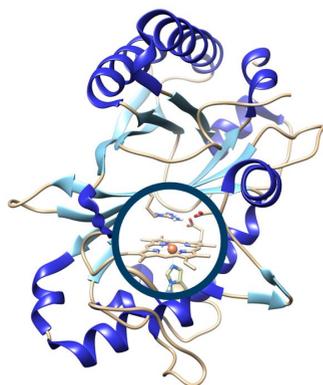


## Fascinating features in *KpDyP* Probing a dye-decolorizing peroxidase using EPR

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Dye-decolorizing peroxidases (DyPs) are heme *b*-containing proteins that occur in the genomes of several fungi and bacteria. As is the case with other members of the peroxidase-chlorite dismutase superfamily, DyPs express a ferredoxin-like fold to which the heme group is linked by a histidine residue. DyPs can be divided into three distinct classes (A, B, C) and are able to degrade a wide range of substrates, including textile dyes and lignin. This makes them interesting for biotechnological applications such as waste water treatment and biofuel production. However, a fairly low peroxidase activity is reported with conventional substrates compared to other peroxidases, challenging the physiological function of this

family<sup>1</sup>.

Here, multi-frequency CW and pulsed EPR was used to study *KpDyP*, a dye-decolorizing peroxidase from the human pathogen *Klebsiella pneumoniae*, recombinantly expressed in *E. coli*<sup>2</sup>. The study focused on both wild-type *KpDyP* and different variants, allowing to characterize the role of key amino-residues in the protein. Fascinating results include the observation of a large heterogeneity and flexibility of the heme pocket, formation of a Compound I porphyrin radical during enzymatic turnover and an unusual stable organic radical found in the resting state of the enzyme. Moreover, we gained insight in the role of the residues Arg232 and Asp143 in the distal part of the heme pocket.

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## Muti-Extreme THz ESR -Current Status and Future-

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We have been developing THz ESR under multi-extreme conditions in Kobe, which covers the frequency region between 0.03 and 7 THz<sup>1</sup>, the temperature region between 1.8 and 300 K<sup>1</sup>, the magnetic field region up to 55 T<sup>1</sup>, and the pressure up to 1.5 GPa<sup>2</sup>. Current status of the developments and some results using our THz ESR under extreme conditions will be discussed. Firstly, we will show our recent developments of the torque magnetometry<sup>3</sup> and mechanically detected ESR<sup>4</sup> measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR<sup>5</sup>. Using this new measurement system, we were able to observe THz ESR of the microliter solution sample (myoglobin)<sup>6</sup>. Secondly, we will show that our pressure region is extended to 2.7 GPa using the transmission-type hybrid pressure cell<sup>7</sup>. We will show our recent development of high-pressure THz ESR system using our hybrid pressure cell, and the 25 T superconducting magnet at IMR, Tohoku University<sup>8</sup>. Finally its application to Cs<sub>2</sub>CuCl<sub>4</sub>, which reveals the pressure dependence of the exchange interactions in the system in collaboration with the Dresden high magnetic field group, will be discussed<sup>9</sup>.

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## Use of EPR spin trap BMPO and KO<sub>2</sub> to study interactions of H<sub>2</sub>S with biologically active compounds

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Endogenously produced H<sub>2</sub>S and polysulfides (H<sub>2</sub>S<sub>n</sub>) in living organisms effect numerous biological processes in which superoxide radical anion (O<sub>2</sub><sup>•-</sup>) and hydroxyl (HO<sup>•</sup>) radicals play an important role. Therefore we used EPR spin trapping technique with BMPO spin trap and KO<sub>2</sub> to study production and/or inhibition of oxygen derived radicals by H<sub>2</sub>S and polysulfides and by their interactions with biologically active compounds.

As detected by the EPR spectra of <sup>•</sup>BMPO-OH, the formation of HO<sup>•</sup> in physiological solution or by decomposition of H<sub>2</sub>O<sub>2</sub> was found in the presence of H<sub>2</sub>S and H<sub>2</sub>S<sub>4</sub>. The EPR spectra of <sup>•</sup>BMPO-OOH/OH spin-adducts monitored using Na<sub>2</sub>S or Na<sub>2</sub>S<sub>2</sub> in a mixture with doxycycline antibiotic, depending on ratio, concentration and time, displayed the bell-shape kinetics in terms of producing/scavenging superoxide and hydroxyl radicals and decomposing hydrogen peroxide. The effects were significantly higher in comparison when H<sub>2</sub>S or doxycycline acted alone.

From KO<sub>2</sub> dissolved in DMSO, O<sub>2</sub><sup>•-</sup> was trapped forming <sup>•</sup>BMPO-OOH spin-adducts. We observed that the amount of the trapped O<sub>2</sub><sup>•-</sup> was inhibited by H<sub>2</sub>S<sub>4</sub> >> H<sub>2</sub>S, but not by the water-soluble vitamin E derivative trolox or by glutathione. As detected in the EPR spectra of BMPO spin-adducts, H<sub>2</sub>S during interaction with selenite (Na<sub>2</sub>SeO<sub>3</sub>) (but not selenate, Na<sub>2</sub>SeO<sub>4</sub>) significantly decreased O<sub>2</sub><sup>•-</sup> and HO<sup>•</sup> radical concentrations in comparison when H<sub>2</sub>S or selenite acted alone.

The results imply a direct involvement of H<sub>2</sub>S and its derivatives in O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub>/HO<sup>•</sup> free radical pathways modulating the antioxidant/toxic biological processes. It is underlined that the products of interaction of H<sub>2</sub>S and its derivatives with biologically active compounds as H<sub>2</sub>O<sub>2</sub>, selenite or doxycycline may explain several biological effects of these compounds.

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## EPR studies of Cu(tn)Cl<sub>2</sub> - the low-dimensional Heisenberg antiferromagnet with $S = 1/2$

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Theoretical studies show that for sufficiently weak interlayer coupling  $J'$ , a typical sharp  $\lambda$ -like peak in the specific heat marking the onset of three-dimensional (3D) long-range order (LRO) completely vanishes and despite the existing 3D LRO, the specific heat follows the behavior of the 2D system. Such extreme weakness of  $J'$  was experimentally observed in Cu(tn)Cl<sub>2</sub> (tn = C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>). The compound crystallizes in orthorhombic space group Pna21,  $a = 17.956 \text{ \AA}$ ,  $b = 6.859 \text{ \AA}$ ,  $c = 5.710 \text{ \AA}$ ,  $Z = 4$ . The structure consists of covalent ladders running along the  $c$  axis. The studies<sup>1</sup> of the polycrystalline Cu(tn)Cl<sub>2</sub> identified the compound as an  $S = 1/2$  2D HAF magnet with the effective intralayer exchange coupling,  $J^{\text{eff}}/k_B \approx 3 \text{ K}$ . Single-crystal studies of EPR spectra were performed from 1.5 to 300 K using the X-band (commercial BRUKER E 500 spectrometer) and homemade spectrometer (from 50 to 150 GHz). Angular dependence of resonance fields at 300 K revealed nearly constant  $g$ -factors within the  $ab$  plane with extremal values along the  $a$  and  $b$  axis ( $g_a = 2.051$ ,  $g_b = 2.052$ ). The differences enlarged with lowering temperature due to the decrease of  $g_a$  down to 2.030 at 2 K, while  $g_b$  remained constant at all temperatures. Other extremal value was found in  $ac$  plane along the  $c$  axis which coincides with the  $z$  axis of the  $g$ -tensor. The extremal  $g$ -values in the  $ab$  plane were not found along the local crystal field  $x$ ,  $y$  axes which deviate from the  $a$  and  $b$  axis by the angle  $45^\circ$ . The analysis of temperature dependences of  $g_c$  on  $g_a$  performed within the model of dipolar chain found excellent agreement with experimental  $g$ -factors in the interval between 10 and 100 K. The deviations below 10 K coincide with the deviations from the Curie-Weiss law due to the onset of short-range correlations while above 100 K, a strange increase of both  $g$ -factors appears. Similar tendency was observed in the temperature dependence of EPR linewidth along the  $a$  and  $c$  directions where instead of a mild linear increase expected from the spin-phonon coupling, very steep increase is observed above 100 K with a plateau above 200 K. Complementary specific heat measurements in  $B = 0$  revealed a tiny peak at about 160 K which can be associated with the structural phase transition removing disorder in the carbon positions reported for the high-temperature phase. Angular variation of  $\Delta B$  within the  $ac$  and  $ab$  planes reflects the presence of spin anisotropies and spin diffusion. The high-frequency spectra in  $B \parallel a$  suggest the presence of the alternating Dzialoshinskii-Moriya interaction which is allowed by the symmetry. In future, more detailed studies of EPR as well as AFMR spectra will be performed to obtain information about the spin anisotropies in Cu(tn)Cl<sub>2</sub>.

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## EPR Characterization of Ti (III) Species in Heterogeneous Ziegler-Natta Catalysts

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Ziegler-Natta catalysts are based on a pre-catalyst formed by TiCl<sub>4</sub> supported on high surface area MgCl<sub>2</sub> and activated by a co-catalyst consisting of a main group metal alkyl (generally an aluminum alkyl). Due to significant cost benefits, these systems remain dominant in the production technology of polyolefins.<sup>1</sup> In a Ziegler-Natta system, the co-catalyst acts as reducing activating agent, generating paramagnetic Ti (III) species featuring a metal-carbon bond. These are presumed to be the active species even though a detailed molecular structure description is still missing.<sup>2</sup> Therefore, deeper research on the paramagnetic active sites of the Ziegler-Natta catalysts is of crucial importance to implement the efficiency of the catalyst. In this work preliminary continuous wave and pulse EPR experiments performed on pre-catalysts prior and after activation at X- and Q- band frequencies are presented to get a microscopic description of the coordination sphere of Ti (III) species<sup>3-5</sup>.

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## Conformations of dinitroxides and the exchange coupling – is the interaction intra- or intermolecular?

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Stable organic radicals, such as nitroxides, find potential usage in many applications, e.g. spin probes in membrane research or as contrast agents in magnetic resonance imaging. Polynitroxides with multiple unpaired spins show enhancement of NMR signal through dynamic nuclear polarization<sup>1</sup>. The crucial role in this process is played by the mutual orientation of nitroxide moieties. Despite the evidence of intra- and intermolecular exchange interactions from several ESR measurements, the mechanism and the temperature-dependent dynamics on the molecular level is hardly reproducible. In our work, we shed more light into this topic using Density Functional Theory with broken symmetry approach<sup>2,3</sup>. We show that in certain cases a theoretical structure corresponding to the high observed exchange is too constrained thus rather inter- than intramolecular interaction may be considered. Dependence of the mutual orientation on the exchange coupling constant  $J$  is presented as an overview of the theoretical configurational possibilities. It is evident that the data calculated for the lowest energy conformation are far from the dynamic experimental system at normal temperatures. As seen from experiments, a solvent also significantly affects the ESR observables. We propose a methodology involving molecular dynamics to address these issues.

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## EPR spectroscopy and Spectroelectrochemistry of New Water-Soluble Copper(II) complexes with Morpholine-Thiosemicarbazone Hybrids

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In a continuous effort to improve the bioavailability and therapeutic profile of thiosemicarbazones (TSCs) and Cu(II)-TSC complexes, novel thiosemicarbazone hybrids with bioactive L-proline, homoproline, piperazine or iminodiacetate moieties were recently prepared using molecular hybridization approach. The attachment of N-substituted morpholine moiety at the TSC backbone resulted in a simultaneous improvement of aqueous solubility and cytotoxicity.<sup>1</sup> It was shown that new compounds were 2–5 fold more toxic towards cancer cells than healthy cells. The coordination of TSCs to Cu(II) resulted in Cu(II)-TSC complexes with similar or improved antiproliferative activity. Thus, our study showed that attachment of morpholine moiety at the TSC backbone and the subsequent coordination to Cu(II) resulted in new drug candidates, likely with better therapeutic profile than Triapine and a great potential for further clinical development. The observed 50% Tyrosyl radical quenching could be rationalized by the fact that the proligands act as tridentate iron chelators forming 1:2 iron-to-ligand complexes. To investigate whether the biologically accessible reduction of new complexes is metal-centered, the reversible one-electron reduction was studied by in situ UV–vis-spectroelectrochemistry. The spectral changes of the S→Cu(II) charge transfer bands (~425 nm) clearly confirmed the reduction of Cu(II) to Cu(I). To confirm the involvement of copper(II) in the reduction processes, in situ EPR electrochemistry was performed, since metal-based reduction would result in the formation of EPR-silent Cu(I) species. A significant decrease of EPR signal was observed in accord with the formation of diamagnetic Cu(I) d<sup>10</sup> complex. For aqueous solutions the reversibility was significantly reduced, implying a more complex mechanism involving the release of the proligand.

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## Triplet states of Donor-Acceptor porphyrins

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

Transient EPR spectroscopy in combination with pulse ENDOR has previously been employed to characterize the photo-generated triplet states of linear and cyclic zinc porphyrin oligomers.<sup>2a</sup> Studies have also explored the influence of the bridging linker,<sup>2b</sup> where varying the length or geometry of a *meso-meso* linker, imposes constraints on the dihedral angles between adjacent porphyrin rings. In addition, the significance of symmetry was explored by altering the distribution of side groups in porphyrin oligomers thus rendering the porphyrin units inequivalent; this work demonstrated how the symmetry of the porphyrin changes the triplet state delocalization.<sup>2c</sup>

In this work, we extend the investigation of structure-property relations to the photo-generated triplet states of a series of linear zinc porphyrin systems with donor-acceptor *meso* groups. Transient CW, magnetophotoselection and pulse ENDOR spectroscopies have been used to explore and gain a better understanding of the ZFS and HFC. These magnetic parameters ultimately depend on the shape and distribution of the triplet spin density. Preliminary results have so far provided information into how different combinations of donor- acceptor groups can influence the triplet state wavefunction. Rationalization of the experimental trends have been performed in combination with of DFT and CASSCF calculations.

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## Excited quartet state formation in porphyrin-trityl compounds: spectroscopic evidence & mechanistic details

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A fundamental understanding of the spin dynamics in organic multi-spin systems is essential to the development of organic spintronic devices and could provide a basis for the development of new information processing strategies.<sup>1</sup> To be able to control the spin dynamics on a molecular level, we require a profound knowledge of the structure-function relationships in organic systems that can create, store, and transfer spin-information.

Here we investigate spin-information transfer in a series of covalently linked porphyrin-trityl compounds<sup>2</sup> by EPR and optical spectroscopies. After photoexcitation of the chromophore, excited quartet state formation is observed at cryogenic temperatures. Such quartet formation was observed before in related systems<sup>3-5</sup> and is mediated by the strong exchange interaction between the porphyrin triplet and the trityl radical. At ambient temperature, the strong interaction between the two spin centres is evidenced by ultrafast quenching of the porphyrin excited state. Combining the results from optical spectroscopy and transient EPR experiments, we shed light on the mechanism of quartet formation in this strongly coupled spin system.

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## First Demonstration of Magnetoelectric Coupling in a Molecular Nanomagnet: Single-Crystal EPR studies of $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_3](\text{ClO}_4)\cdot\text{py}$ under static electric fields

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Single-crystal EPR experiments show that the highly symmetric antiferromagnetic half-integer spin triangle  $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_3](\text{ClO}_4)\cdot\text{py}$  (**1**) possesses a  $S_T = 1/2$  ground state exhibiting high g-anisotropy due to antisymmetric exchange (Dzyaloshinskii-Moriya) interactions. EPR experiments under static electric fields reveal that this ground state couples to externally applied electric fields. This magnetoelectric coupling causes an increase in the intensity of the intradoublet EPR transition and does not affect its resonance position when  $B_0 \parallel z$ . The result is discussed on the basis of theoretical models correlating the spin chirality of the ground state with the magnetoelectric effect.

## Nature and Topology of Metal-Oxygen Binding Sites in Zeolite Materials

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Catalysis is the key enabling technology of the current chemical industry and heterogeneous (solid) catalysts dominate industrially relevant processes. Yet the exact nature of the active species is often ill-defined, if not completely unknown. Crucially, reactivity patterns often depend critically on the presence of paramagnetic species. Elucidating the role and influence of such species in catalytic processes is presently one of the most challenging endeavours from both an experimental and theoretical perspective and a limiting step in substituting noble metals with earth abundant elements.

Addressing catalysis complexity is thus one of the major challenges in the quest for a knowledge-driven realization of a sustainable future.

There exist a number of spectroscopic techniques able to inform on the geometric and electronic structure of potentially catalytic active sites, but either they yield information averaged over the bulk sample or lack description of the intimate features of chemical bonding, which include covalency, ionicity, electron and spin delocalization. In this contribution we show how the synergic combination of site-selective isotopic labelling with <sup>17</sup>O and advanced electron magnetic resonance techniques can be used to derive site-specific structural and electronic models of industrially relevant zeolite materials.

## The non-innocent role of spin traps

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DMPO (5,5-Dimethyl-1-pyrroline N-oxide) plays an important role as a spin trap in the EPR study of systems containing free radicals and paramagnetic centers in chemistry and biology<sup>1</sup>. However, since DMPO is often used at high concentrations, it can potentially undergo a significant amount of non-innocent side reactions, not just spin-trapping the radicals. DMPO may even strongly influence the reaction mechanism that one wants to unravel. In this work we investigated the chemical behavior of DMPO in the presence of Cu(II) compounds, which are often used in homogenous catalysis<sup>2</sup>. We have used CW and pulse EPR to study the interaction of Cu(II) with DMPO in DMSO in the absence or presence of competing strong bases. We found that DMPO can coordinate to the Cu(II) ion and we identify the new species by combining the EPR simulations with the density functional theory (DFT) computations.

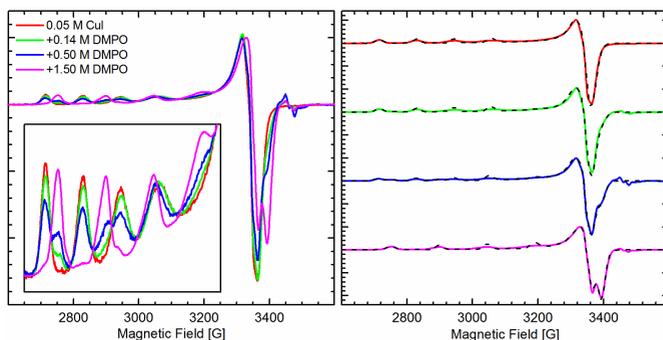


Figure 1 left X-band cw-EPR spectra of 0.05 M CuI in DMSO under the air with increasing concentration of DMPO recorded at 100 K. Each spectra has been normalised to the double integral i.e. total number of spins. right The spectra stacked with corresponding simulated spectra (black dash)

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## Quantum phase transitions in molecular spin systems

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Magnetic interactions between spin centres in molecular materials are influenced by structure, symmetry, chemical path and electronic structure. These properties can be tuned by chemical design, offering an exciting route to achieve materials with spin properties that support new theoretical, experimental, and practical advances in the field of molecular magnetism. We performed electron spin resonance (ESR) at several frequencies in molecular Cu(II) compounds to probe the magnitude of spin-spin interactions. We demonstrate how detailed angular sweep measurements in single crystal samples are a powerful technique to detect intermolecular interactions in the range of mK even at room temperature, an achievement that would require refined experimental conditions to be obtained by other techniques such as magnetic susceptibility measurements. Paramagnetic sites lacking an inversion centre present crossing of transitions where a dynamical quantum phase transition between an isolated-spins regime to a coupled-spins regime takes place. This transition manifests as the merging of absorption lines in an angular range that depends on the exchange coupling. On the other hand, the exchange narrowing theory enables the detection of magnetic interaction between sites related by an inversion centre by modelling the modulation of the linewidth due to the exchange frequency. The magnetic parameters were compared between different samples and correlated with their structure. Broken-symmetry density functional theory (BS-DFT) was applied for calculating the exchange couplings and compared to the experimental results with reasonable agreement. In conclusion, our results provide a protocol for probing magnetic interactions and detecting entangled spin phases in metallic molecular materials.

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## EPR investigation of a tyrosine dyad in a ribonucleotide reductase-inspired model system

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Amino acid radicals are involved in essential processes in primary metabolism such as photosynthesis, respiration, and biosynthesis of DNA building blocks. They serve as one-electron redox cofactors in biocatalysis and multistep proton-coupled electron transfer (PCET) reactions. *E. coli* class Ia ribonucleotide reductase (RNR), which catalyzes the reduction of nucleotides to their corresponding deoxynucleotides, is a paradigm for studying PCET in biology. The radical transfer mechanism in RNR involves at least five tyrosine residues. A  $\pi$ -stacked, cofacially aligned tyrosine dyad is required for the fidelity of the radical transfer during PCET, and thus of the catalytic activity.<sup>[1]</sup> The remarkable structure of the two tyrosines might affect the redox chemistry in a way that they do not provide two sequential radical transfer steps but act as a collective property.

In this work, we used pulsed EPR and orientation selective <sup>1</sup>H/<sup>2</sup>H ENDOR to investigate whether the perturbed redox properties of the tyrosines is due to the shared hydrogen bond within the dyad. We used a model system, called DPX, that mimics the tyrosine dyad in RNR. In DPX two phenols are cofacially positioned at a fixed distance on a xanthene backbone. Pulsed EPR showed the phenoxy radical could be generated and trapped after photoirradiation with a 266 nm lamp. Combination of orientation selective ENDOR data, their corresponding simulations and DFT calculations revealed the existence of a hydrogen bond that is perpendicular to the aromatic ring plane. Our results strongly support that the non-covalent interaction between two tyrosines perturbs the well-studied one-electron redox chemistry of tyrosine radical in RNR. Here we report the first example that suggests a collective act of a tyrosine pair in an enzyme.

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## Automated Alignment of a Quasi-Optical Table for a HFEPR Spectrometer

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A quasi-optic system is a common part of High Frequency Electron Paramagnetic Resonance (HFEPR) spectrometers. A main purpose for its use is to achieve low losses of a microwave signal<sup>1</sup> in a wide range of frequencies, which is beneficial for a pulsed and a multi-frequency<sup>2</sup> operation. However, a gaussian beam of microwaves has to be at some point transmitted into a probe-tube that is attached into superconducting magnet. A good coupling between the quasi-optic system and the probe-tube is therefore necessary. Usually, it is done by a tiresome manual adjustment of quasi-optic system into just right position, each time when a new sample is loaded, or the probe-tube is exchanged. To simplify this procedure, an automated alignment system was embedded into a newly constructed HFEPR spectrometer. It consists of five high precision servo drive mechanisms to allow three-dimensional position adjustment along an elevation adjustment of a whole quasi-optical table. The positioning system is controlled by a computer software that will do the tiresome adjustment procedure instead of operator.

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## Mechanistic insight in peroxidase activity towards industrial applications

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The incorporation of proteins in mesoporous materials provides a promising tool to create new hybrid materials for biosensing or biocatalysis applications. Although such an incorporation of the enzyme in a porous material can lead to increased stability of the protein, it is not trivial to find the optimal enzyme-matrix match. In some cases, interaction with the surface of the inorganic host will cause protein unfolding and incorporation is strongly influenced by the buffer<sup>1</sup>. In the frame of the European Programme MSCA-Horizon 2020 "Paramagnetic Species in Catalysis Research (PARACAT)", we focus on the incorporation of heme peroxidases in porous titania and silica. The project targets at gaining insight into the catalytic mechanism of selected peroxidases using EPR techniques and at designing novel protocols in order to incorporate the proteins into nanoporous materials, with the perspective of enhancing their stability and catalytic efficiency. Heme peroxidases constitute a large and variegated protein superfamily, whose activity was first observed and described in scientific literature more than two centuries ago. These enzymes, which feature a heme *b* prosthetic group in their active-site, are able to oxidize a range of different substrates in 1- or 2- electron(s) transfer reactions, using hydrogen peroxide as a cofactor. Members of this superfamily have also been shown to possess catalase-like, peroxygenation and chlorite decomposition (generating Cl<sup>-</sup> and O<sub>2</sub>) mechanisms<sup>2</sup>. Our current work focuses on the characterization of chlorite dismutase from the nitrate respirer *Nitrobacter Winogradskyi* (NwClD)<sup>3</sup>. Horseradish peroxidase is used as a comparison and control protein to test different incorporation techniques. First protocol outlines and EPR results will be shown.

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## **NO<sub>2</sub> adsorption in porous metal organic frameworks (MOFs) investigated by electron paramagnetic resonance**

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Toxic air pollutants, such as NO<sub>x</sub>, SO<sub>x</sub>, CO, H<sub>2</sub>S, NH<sub>3</sub>, are released to the environment due to burning fossil fuels and other human activities. In addition to contributing to smog, acid rain, global climate change, and ozone depletion, among other devastating effects air pollution causes 7 million premature deaths annually: one eighth of total global deaths (WHO). Oxides of nitrogen (NO<sub>x</sub>) and sulphur (SO<sub>x</sub>) are major components of smog, with NO<sub>x</sub> being the most toxic. The most prevalent NO<sub>x</sub> is NO<sub>2</sub> (nitrogen dioxide) is highly corrosive, causing severe respiratory diseases. Thus, the capture of such pollutants is a pressing scientific problem. Reversible physisorption of NO<sub>2</sub> in highly adsorptive porous materials could be a promising approach to mitigate NO<sub>x</sub> pollution. The major challenge is to find suitable materials that are inert to degradation under the attack of such highly reactive, oxidising and corrosive gases. Porous materials such as zeolites, metal oxides, mesoporous silica and activated carbons suffer from low capacities and often induce irreversible decomposition of NO<sub>2</sub>, coupled with degradation of the host.

One promising approach is the use of robust metal organic frameworks as NO<sub>2</sub> adsorbents. However, no MOF system was demonstrated so far to reversibly adsorb NO<sub>2</sub>, despite clear evidence of NO<sub>2</sub> retention in metal organic frameworks. Recently, the Manchester group has discovered several very stable MOFs that are good CO<sub>2</sub> and NO<sub>2</sub> adsorbents. They have made the first observation of isotherm adsorption of pure NO<sub>2</sub>, in a robust aluminium MOF, MFM-300(Al). This presentation will discuss the first pulsed EPR studies focusing on the reversible adsorption of NO<sub>2</sub> in an ultra robust metal-organic framework, MFM-300(Al)<sup>1</sup>. The NO<sub>2</sub>...MOFs interactions were studied by a combination of continuous wave and pulsed EPR methods, which provided valuable insights into the adsorption mechanisms. The NO<sub>2</sub> uptake is fully reversible, and the host material can be regenerated with full retention of its structure and sorption capacity for at least five cycles.

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## Towards highly sensitive EPR of various paramagnetic systems at mK temperature

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Major advances are currently being made in the area of cavity quantum electrodynamics and the development of superconducting quantum circuits which can offer a significant improvement in the EPR sensitivity<sup>1</sup>. These include recent developments of the ultrahigh-Q superconducting microresonators, quantum-limited cryogenic microwave amplifiers and the use of millikelvin temperatures accessible in dilution refrigerators<sup>2,3</sup>. The combination of such developments has already led to the record-breaking EPR sensitivity of 65 spins/ $\sqrt{\text{Hz}}$ <sup>4</sup>. However, these demonstrations have typically studied paramagnetic impurities within the substrates on which the superconducting resonators are patterned<sup>1-4</sup>. Here, we discuss the potential of extending the use of highly sensitive EPR at millikelvin temperatures, making use of both 3D cavities and patterned microresonators to study a broader and more general set of systems including spin labels and various intrinsic paramagnetic centers in solid state and biological compounds.

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## Temperature dependent EPR spectra of Cu<sup>2+</sup> doped (NH<sub>4</sub>)<sub>2</sub>[Zn(NH<sub>3</sub>)<sub>2</sub>CrO<sub>4</sub>]<sub>2</sub><sup>1</sup>

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Orientalional disorder in ionic solids is a common occurrence<sup>1</sup>. Cu<sup>2+</sup> doped (NH<sub>4</sub>)<sub>2</sub>[Zn(NH<sub>3</sub>)<sub>2</sub>CrO<sub>4</sub>]<sub>2</sub> was investigated by means of electron paramagnetic resonance (EPR) spectroscopy. Powder X-band EPR spectra of Cu<sup>2+</sup> doped (0.3 mole %) (NH<sub>4</sub>)<sub>2</sub>[Zn(NH<sub>3</sub>)<sub>2</sub>CrO<sub>4</sub>]<sub>2</sub> were measured in the temperature range 100 – 298 K. It has been shown that the unpaired electron of Cu(II) ion is in the *d*<sub>z<sup>2</sup></sub> orbital showing axial destabilization of the copper(II) environment. At low temperature, spectra show resolved super-hyperfine splitting due to nitrogen atoms originating from the NH<sub>3</sub> ligands. It has been described that NH<sub>3</sub> molecule has considerable freedom of rotation about its threefold axis<sup>2</sup>. Temperature dependent spectral changes have been related to the orientational order-disorder transition occurring at 275 K.

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## Photonic Band Gap Resonators For High Field EPR of Films and Thin Film Materials

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Flat layered materials ranging in thickness from about a nanometer to several micrometers enabled a wide range of technological applications and breakthroughs from electronic semiconductor devices and abrasive/hard coatings to thin-film solar cells and batteries. Large efforts have been also put towards improving pain coating and polymer films as well as understanding biofilm formation.

While EPR is a well suited analytical tool for studying many of the abovementioned system, often a problem arises with accommodating thin flat sample geometry by conventional EPR resonators. Although some arrangements could be made to place sample into X-band resonators because of a relatively large (up to ca. 9-10 mm in diameter) access hole, EPR experiments at high magnetic fields / high frequencies are much more challenging because dimensions of single-mode resonators generally scale down with the wavelength of the electromagnetic radiation. Flat samples could be also accommodated by Fabry-Perot resonators but such structures generally have low finesses and are challenging to tune. Recently, we have introduced a radically new line of millimetre wave resonators that is based on one-dimensional (1D) photonic band gap (PBG) dielectric crystals.<sup>1,2</sup> The PBG crystals are assembled from  $\lambda/4$  low-loss dielectric layers with alternating dielectric constants and a flat EPR sample forms a defect which concentrates mm-wave  $B_1$  field. The prototype PBG resonators constructed for W-band (94.3 GHz) EPR demonstrated experimental Q-factors from  $\approx 520$  to  $\approx 3,300$  depending on dimensions and sample loading. Geometry of 1D PBG resonators is ideally suited for flat samples with thickness  $< 50$  micron depending on the dielectric constant and the loss tangent. Thicker non-lossy flat samples could also be studied if the resonator is tuned to a higher mode. For aqueous samples we employed a nanoporous anodic aluminium oxide disc of  $50 \mu\text{m}$  in thickness to provide for overall ca. 2-3  $\mu\text{l}$  sample volume. Such a configuration increases concentration sensitivity of W-band EPR for liquid aqueous samples by at least tenfold when compared with high-Q ( $\approx 3,000$ ) cylindrical  $\text{TE}_{012}$ -type cavity. Experimental tests of the new resonators for aqueous and polymer thin film samples are also reported. Supported by the National Institutes of Health 1R21EB024110.

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## Ultra High Vacuum transfer chamber for High Field – Electron Paramagnetic Resonance

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Motivated by the broad area of application including quantum computing, optoelectronics, or sensor technology, the interest in a detailed description of microscopic processes in molecular nanomagnets (MNMs) deposited on surfaces has been increasing continuously.<sup>1</sup> Unfortunately, many MNMs on surfaces are sensitive to oxidation and decomposition under normal ambient conditions.<sup>2</sup> Therefore, minimizing the detrimental effects and preventing the formation of products of decomposition is a crucial step in the fabrication and characterization process. In this work, we present the set up and development of a general multi-purpose transfer system that will allow transporting air sensitive samples from an evaporation chamber to a spectrometer probe without exposure to atmospheric conditions. The transfer system connects our home-built high field electron paramagnetic resonance (HF-EPR) spectrometer with the in-house ultra-high vacuum (UHV) cluster located within the Nanofabrication and Characterization Facilities of the Central European Institute of Technology (CEITEC). Our HF-EPR spectrometer is based on rapid frequency scans that operate at frequencies between 80 GHz to 1100 GHz, at temperatures from 1.8 K to 300 K, and at magnetic fields up to 16 T. The high sensitivity of our EPR setup allows detecting small concentrations of paramagnetic molecules, and confirming the successful deposition and intactness of molecules on surfaces based on their magnetic properties. The design consists of a portable vacuum suitcase dedicated EPR airlock and an EPR sample holder that allows sample transferring from any UHV chamber with ConFlat (CF) flange into our highly precise HF-EPR spectrometer. Furthermore, our sample holder design contains electric contacts, temperature sensor, and heater for complex EPR experiment. The high spectral resolution achieved by higher magnetic fields and higher frequencies along with the proposed here handling system enables exploring spin dynamics and other phenomena not accessible by the current commercially available technologies.

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## Electron Paramagnetic Resonance (EPR) Study of Battery and Functional Materials

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EPR spectroscopy and related hyperfine techniques provide a powerful insight into the characterisation of solid-state materials. A diverse array of paramagnetic species is typically present in a material, including rare earth or transition metal complexes, inorganic radicals and point defects, which directly facilitate its function and efficiency. This presentation is intended to provide a few examples of how multi-frequency (X-, Q-, W-band) continuous wave (CW) EPR, ENDOR and pulsed (X-band) techniques, have been employed to provide a deeper understanding of functional materials. The applications of EPR are illustrated for two principle topics currently under investigation:

### i) Electrode materials for Li-ion batteries

Identification and analysis of active sites, defects and transition metal containing impurities in olivine LiFePO<sub>4</sub> cathodes, and lithium titanate-based anode materials that directly influence Li-ion storage and transport. Structure-activity relationship of the materials were evaluated for different precursors, compositions and states-of-charge. A home-built in situ electrochemical cell has been developed to determine changes in oxidation state, formation of performance-inhibiting phases, and transient radical species during operation.

### ii) CaS: Eu phosphors

CaS: Eu phosphors are fluorescent materials with a wide range of applications. They have been shown to possess several paramagnetic features, including Eu<sup>2+</sup>, defects such as F<sup>+</sup> centres, and Mn<sup>2+</sup> impurities. Their nature and concentration have been evaluated and are shown to be highly sensitive to synthetic methods, including choice of precursors, preparation and post-synthesis treatments, which act to influence function and stability of the material.

## Colossal Quadrupolar Couplings in Transition Metal Dithiolene Complexes

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Structural characterization of a charge-neutral tris(dithiolene)rhenium compound produced the first example of a molecular complex with trigonal prismatic geometry. The origin of the hitherto unknown geometry stems entirely from the redox-activity of dithiolene ligands.<sup>1,2</sup> The esoteric electronic structure is revealed by an amazing EPR spectrum that is dominated by the quadrupolar interaction. The only other example of this electronic phenomenon is observed in square-planar bis(dithiolene) complexes of gold, where again the hyperfine coupling is dwarfed by a colossal quadrupolar interaction.<sup>3</sup>

The bis(dithiolene)gold complex represents a model for an organic molecular electron spin qubit attached to a 'metallic' surface.<sup>3</sup> The spin dynamics of this system is examined by pulsed EPR spectroscopy to give the longest coherence lifetime for a molecular qubit possessing a heavy transition metal.

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## Spin probe mobility in relation to free volume and relaxation dynamics: *cis-1,4-(poly)isoprene*

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The structural-dynamic state of amorphous systems is usually characterized by internal probe techniques, such as diffraction, scattering and relaxation, e.g., dielectric spectroscopy.

Here we present the non-direct characterization, the reorientation dynamics of small spin probe 2,2,6,6-tetramethylpiperidinyl-1-oxyl (*TEMPO*) in polymer 1,4-*poly(isoprene)* (1,4-*PIP10k*) from electron spin resonance (ESR) and the free volume of 1,4-*PIP10k* from positron annihilation lifetime spectroscopy (PALS) in relation to the high-frequency relaxations of 1,4-*PIP10k* using light scattering (LS) as well as using broadband dielectric spectroscopy (BDS). Recently, a combined ESR, PALS and BDS work on oligomer *cis-1,4-poly(isoprene)* (1,4-*PIPO.8k*) consisting of twelve monomers per chain was reported.<sup>1</sup>

The spectral simulation of spin system 1,4-*PIP10k/TEMPO* over a wide temperature range from 100 K up to 350 K revealed five regions of different mobility of *TEMPO*, i.e. two mild decreases within slow and fast regime at  $T_{x1}^{\text{slow}}$ ,  $T_{x2}^{\text{slow}}$ ,  $T_{x1}^{\text{fast}}$  then the slow to fast motion regime transition region at  $T_c$  and finally, the two fast sub-regimes at  $T_{x1}^{\text{fast}}$ . These findings are in good coincidence with the characteristic PALS bend effects at  $T_g^{\text{PALS}}$ ,  $T_{b1}^{\text{L}}$  and  $T_{b2}^{\text{L}}$ . The comparison of the ESR and PALS findings was related with the results on oligomeric 1,4-*poly(isoprene)* (1,4-*PIPO.8k*)<sup>1</sup>. Finally, the time scales of the slow and fast motion regimes of *TEMPO* in 1,4-*PIP10k* compared with the six slow and fast relaxation modes from BDS<sup>2</sup>, LS and NS techniques revealed that the spin probe mobility over a wide temperature range is influenced by the local dynamics of the modified local surroundings of *TEMPO* probe which reflects the structural-dynamic changes of 1,4-*PIP10k*.

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## Planarity versus Non-planarity of the Imidazoline Ring in Radical Ions of a Molecular Candidate for Singlet Fission

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Singlet Fission (SF) represents one of the promising ways how to enhance performance/increase efficiency of the solar cells. During this process two triplet (T) excitons from one singlet (S) exciton and a ground-state molecule is generated. Molecular candidates for SF require similar  $S_0-T_1$  and  $T_1-S_1$  gaps and therefore, many laboratories are “hunting” for suitable structures.<sup>1</sup> A structural motif of diamino-quinone derivative was found to meet the basic requirements of singlet-triplet gap<sup>2</sup> (described above) and the study was extended to its derivative 1,2,2,3-tetramethyl-2,3-dihydro-1H-naphtho[2,3-*d*]imidazole-4,9-dione, which is preferred due to the following features. It prevents significant amino group twisting and ensures the absence of mobile protons, suppressing intermolecular hydrogen bonding and tautomerization by nitrogen-to-oxygen proton transfer in excited states.<sup>3</sup>

However, for application in solar cells, not only photophysical behavior but also the redox properties and stability of the corresponding redox forms are important to be investigated. Therefore we've been focused on the open-shell structures (radical ions) of the above-mentioned naphtho-imidazole-dione. The results from combined EPR spectroelectrochemical experiments and DFT calculations have provided an interesting structural information on the different planarity of imidazoline ring in the radical ions in diluted electrolyte solution.<sup>4</sup> The latter as well as the stability of both radical ions will be discussed.

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## EPR Studies of $\{(C_2H_{10}N_2)[Cu(C_{10}H_2O_8)] \cdot 2.5H_2O\}_n$ - a Quasi-Two-Dimensional $S = 1/2$ Antiferromagnet

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The analysis of magnetization and heat capacity identified the title compound as a quasi-two-dimensional  $S = 1/2$  Heisenberg antiferromagnet on the rectangular lattice. A phase transition to a magnetically ordered state has been observed in zero magnetic field at  $T_N = 1.28$  K. Magnetic susceptibility and heat capacity measurements establish the intralayer exchange couplings,  $J_b/k_B \approx 7.5$  K and  $J_c/k_B \approx 3.15$  K along the  $b$  and  $c$  directions, respectively. The analysis of magnetic specific heat in non-zero magnetic fields revealed features characteristic for a field-induced Berezinskii–Kosterlitz–Thouless transition theoretically predicted for ideal two-dimensional magnets.

The crystal structure of  $\{(C_2H_{10}N_2)[Cu(C_{10}H_2O_8)] \cdot 2.5H_2O\}_n$  determined at 100 K is monoclinic, space group  $P2_1/c$  with the unit cell parameters  $a = 7.3937$  Å,  $b = 18.4414$  Å,  $c = 11.3607$  Å,  $\beta = 94.783^\circ$ , and  $Z = 4$ . The  $Cu^{2+}$  ions form nearly flat  $CuO_4$  plaquette units connected into a two-dimensional framework through anions of the pyromellitic acid  $[C_6H_2(COO)_4]^{4-}$  and build layers in the  $bc$  plane. The ethylenediamine cations and molecules of waters are located between these layers and are connected to the anionic framework  $[Cu(C_6H_2(COO)_4)]^{2-}$  through hydrogen bonds. Dipole-dipole and van der Waals interactions are also effective in the molecular packing. Electron paramagnetic resonance (EPR) measurements of a powder sample have been performed in the X-band range (Bruker ELEXSYS E500) at a fixed frequency of 9.4 GHz in the temperature range from 2 K to 300 K in magnetic fields up to 0.5 T. A spherical sample with a diameter of about 1 mm was formed by using GE 7031 varnish and was glued on a Suprasil-quartz rod.

The analysis of  $g$ -factor confirmed, that in the temperature range from 300 to 25 K  $g$ -factors change monotonously, there is a decrease of all components with decreasing temperature. This behaviour could be related to a general contraction of the crystal structure. However, at temperatures below 25 K significant increase of  $g_x$ ,  $g_y$  and decrease of  $g_z$  was observed. Such a behaviour was experimentally observed in low-dimensional magnets and coincides with the theoretical predictions for the resonance fields in the presence of a dipolar coupling and the exchange anisotropy. The phonon modulation of the spin anisotropies can be responsible for the increase of the EPR linewidth observed above 140 K. On the other hand, the upturn of the linewidth appearing below 30 K can be ascribed to the development of intralayer magnetic correlations.

This work was supported by the projects VEGA1/0269/17 and APVV-18-0197.

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## Structural and EPR properties of Cu(II) complexes bearing $\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}^-$ and 2,2'-bipyridine as ligands

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Only a handful of Cu(II) complexes bearing chalcogenated imidodiphosphinato type of ligands  $\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\}^-$ , E = O, S, have been reported up to now<sup>1-3</sup>. In this work, the synthesis, as well as the structural and spectroscopic characterization of  $[\text{Cu}\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}(2,2'\text{-bipyridine})(\text{X})]$ , X =  $\text{NO}_3^-$  (**1**),  $\text{I}^-$  (**2**),  $\text{PF}_6^-$  (**3**), will be presented. X-ray crystallographic studies revealed that complexes **1**, **2** and **3** exhibit trigonal bipyramidal  $\text{CuO}_3\text{N}_2$ , square pyramidal  $\text{CuO}_2\text{N}_2\text{I}$  and square planar  $\text{CuO}_2\text{N}_2$  first coordination spheres, respectively (Fig. 1). UV-vis and cw EPR spectroscopy studies provided evidence that, in solution, all three complexes exhibit similar tetragonal structures. Furthermore, ligand super-hyperfine interactions of the unpaired electron of complexes **1** and **2** were investigated by ENDOR and HYSCORE spectroscopies.

We would like to thank the Special Research Account of the National and Kapodistrian University of Athens for financial support.

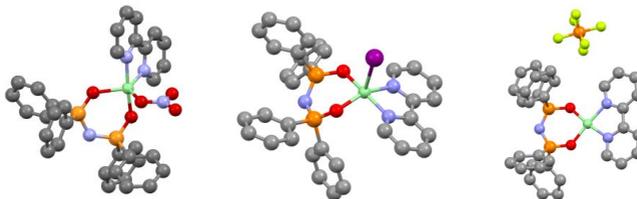


Figure 1: Molecular structure of complexes **1** (left), **2** (middle) and **3** (right). Color coding: Cu (green), O (red), N (blue), P (yellow), C (grey).

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## Using EPR as a tool to investigate copper-catalyzed aerobic benzylic oxygenations

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For a long time, unsustainable oxidants like permanganate and chromic acid derivatives, were used in benzylic oxidation reaction, producing a lot of hazardous waste. Therefore, a shift towards less toxic and more sustainable oxidants has occurred and emphasis is put on developing base-metal catalysed aerobic oxidation reactions.<sup>1</sup> Although considerable progress has been made in this field, the nature of the catalytic species and the mechanistic details of the reaction often remain unclear.<sup>1</sup> Using the examples of Cu<sup>II</sup>-catalyzed benzylic oxygenation of (aryl)(heteroaryl)methanes<sup>2</sup> and copper-catalyzed aerobic oxygenation of benzylopyridine *N*-oxides, the added value of EPR in this field will be demonstrated. The analysis includes the use of continuous-wave EPR and hyperfine techniques. DFT computations corroborate the EPR-spectral interpretations and facilitate the mechanistic interpretations.

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## Metal - metal interactions and spin state preference

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The present poster describes the geometry, electronic structure, energetics and bonding properties of the di-copper (I) and di-chromium (II) acetate diaqua complexes. These studies have been carried out using the single and multireference *ab initio* methods and the DFT method. QTAIM analysis [1] in various spin states was performed using the Gaussian09 [2]. The periodic system QTAIM calculations have been provided via TOPOND utility in the Crystal17 software [3].

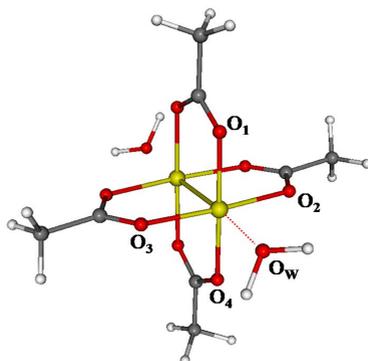


Figure 1. The molecular structure of studied compounds (I) and/or (II) with selected atoms labeling

Acknowledgement: Financial support was obtained from APVV (Project No. APPV-15-0079) and VEGA (Project No. 1/0416/17). We thank the HPC Center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP Project 26230120002, funded by the European Region Development Funds), for computing facilities

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## EPR as a tool to study carrier trapping in persistent phosphors

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Luminescent materials or phosphors are used in many applications such as LEDs or displays. These materials absorb ultraviolet or blue light and convert it into light with a longer wavelength. A special class of luminescent materials, called persistent phosphors, is able to store part of the energy of the excitation light and this energy is then slowly released over the course of minutes or even hours after excitation has stopped. Because of this characteristic afterglow these phosphors are also known as glow-in-the-dark materials, and have by now found their way to important applications such as safety signage in buildings and on planes.

The chemical nature of the defects that are responsible for this afterglow is still largely unknown<sup>1</sup> and this inhibits a systematic approach to optimize the existing phosphors. Many attempts have been made to identify the trapping centres but often these efforts use x-ray absorption techniques<sup>2</sup> which have a large impact on the trapping mechanism itself. In contrast electron paramagnetic resonance offers a way to identify the chemical nature of the traps without using high energy probes such as x-rays or ultraviolet light and without altering the trapping mechanism itself.

For this EPR study we have chosen CaS doped with cerium as a model system because the high symmetry of the host makes it relatively easy to interpret the results, while the paramagnetic dopant Ce<sup>3+</sup> has a low isotropic g-value (1.2985) whose EPR spectrum does not obscure the  $g \approx 2$  region, where signals of trapped electron and hole centres may be expected. The 20 K X-band EPR spectra of as-grown CaS:Ce show that a large fraction of the dopant are incorporated as isotropic Ce<sup>3+</sup> centres, without local charge compensation. Dopant centres with lower symmetry are, however, also observed, indicative of local charge compensation by Ca vacancies. In the  $g \approx 2$  region X- and Q-band EPR spectra reveal the presence of trace Mn<sup>2+</sup> and Cr<sup>3+</sup> impurities and intrinsic defects.<sup>3</sup> Blue light illumination produces an additional EPR component with a g value slightly below the free electron value, which we tentatively assign to electrons trapped at F-centres.

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## ELDOR-detected NMR of exchange coupled systems

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ELDOR-detected NMR is a pulsed EPR technique that is usually applied to measure hyperfine and quadrupole couplings. We recently showed, on the example of Cu(II)-porphyrin dimers, that ELDOR-detected NMR spectra also contain information about electron-electron couplings in the form of anti-holes (*i.e.* signal enhancements, see Figure 1).<sup>1</sup> These spectra can be simulated with a generalized algorithm based on Cox *et al.*<sup>2</sup>

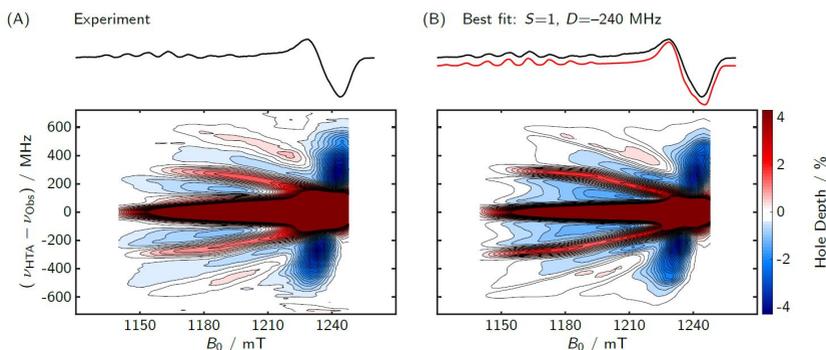


Figure 1: Field-correlated ELDOR-detected NMR spectra of an edge-fused Cu(II)-porphyrin. Adapted from Ref. 1.

In addition to published data, we will show illustrative simulations in order to explain how the electron-electron couplings are encoded in ELDOR-detected NMR spectra. Scientists working with multi-spin or high-spin systems should then be able to judge the usefulness of this approach for their own applications.

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## Sub-micromolar Pulse Dipolar EPR Spectroscopy Shows: Cull-Chelates Label Double-Histidine Motifs More Efficiently with Lower Temperature

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Electron paramagnetic resonance (EPR) distance measurements are making increasingly important contributions to studies of biomolecules underpinning health and disease by providing highly accurate and precise geometric constraints<sup>1</sup>. Combining double-histidine motifs with Cu<sup>II</sup> spin labels shows promise for further increasing the precision of distance measurements<sup>2</sup>, and for investigating subtle conformational changes<sup>3</sup>. It also appeals in proteins containing essential cysteines which can interfere with thiol-specific labelling. However, the non-covalent Cu<sup>II</sup> coordination approach is vulnerable to low binding-affinity<sup>4</sup>. Here, dissociation constants ( $K_D$ ) are investigated *via* modulation-depths of relaxation induced dipolar modulation enhancement<sup>5</sup> (RIDME) EPR distance experiments. The superb sensitivity of these experiments reveals low- to sub- $\mu$ M Cu<sup>II</sup>  $K_D$ s under EPR distance measurement conditions at cryogenic temperatures. Furthermore, extrapolation of room-temperature ITC-determined  $K_D$ s to low temperature using van't Hoff agrees excellently with PDEPR-derived values. We show the feasibility of exploiting the double histidine motif for EPR applications at sub- $\mu$ M protein concentrations in orthogonally-labelled Cu<sup>II</sup>-nitroxide systems.

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