BOOK OF ABSTRACTS

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EquipSent - on the mission to Enable Education Everywhere (P-0)

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EquipSent [1] was founded by ETH students in 2017 as a non-profit volunteer-based association, with the goal to extend the life cycle of scientific equipment and at the same time enhance the quality of education and research around the world by enabling hands-on training on educational institutions with limited financial resources. EquipSent provides a platform to connect donors and recipients in need of scientific equipment used at universities (Fig. 1) and schools. When a successful match has been established, EquipSent facilitates the logistics to transfer the equipment to the recipient institution. Once the devices arrive at the destination, EquipSent stays in contact with the receiver(s) to ensure the equipment is used for education and research purposes and remains functional. We also encourage the donors to stay in contact with the receiver, to establish a multinational collaboration. With our activities, we target three out of the 17 UN sustainable development goals [2], including (1) Quality Education, (2) Industry, Innovation, and Infrastructure (3) Responsible Consumption and Production. In detail, we aim to:

1. **Minimize waste** - by reducing the disposal of out-of-use yet functional scientific equipment.

2. **Improve education** - by supporting universities & schools with limited funding to attain access to functional scientific equipment.

3. **Reduce global inequality** - by establishing collaborations and building a network of research institutions across the world.

In the last year, EquipSent has successfully completed six equipment transfers to countries in South America, Africa, and Asia.

***Figure 1**: Equipment has arrived (left), it is being unpacked (middle) and used (right) in an electronics practical at Université Chretienne Bilingue du Congo (DR Congo, Africa).*

[1] www.EquipSent.org
[2] Transforming our world: the 2030 Agenda, UN Resolution 70/1, **2015**

Method development

Towards Recyclable Hyperpolarization: Design and Performance of a Tabletop DNP Polarizer (P-1)

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The lack of sensitivity remains one of the biggest hurdles in magnetic resonance (MR) applications. The concept of hyperpolarization provides an opportunity to achieve high signal amplitude without relying on large external magnetic fields or long acquisition periods. Twenty years ago, dissolution Dynamic Nuclear Polarization (d-DNP) [1] was introduced providing boosts of more than 10’000-fold in sensitivity. Yet up to this date, the technology still operates in a destructive, single-shot mode meaning that many of the MR spectroscopic capabilities (e.g. multidimensional NMR) are incompatible with state-of-the-art d-DNP methods.

We are presently working at turning d-DNP into a recyclable alternative in synergy with the full potential of NMR spectroscopy. It consists in replenishing the DNP hyperpolarization of a sample flowing through a closed loop, without dilution nor contamination using silica-based material grafted with free electron radicals (HYPSO) as polarizing matrices [2] in a compact and helium-free DNP polarizer coupled to a benchtop NMR spectrometer for liquid-state detection.

Here we will present the current design of the polarizer for now equipped with a cryostat for static measurements, a double-tuned $^{1}H/^{13}C$ probe with a Kα-band microwave generator. We show the performances through the DNP enhancement using water soluble radicals and HYPSO matrices and go deeper in the mechanisms behind polarization transfer from electrons spins to nuclear spins in our specific conditions.

References:

[1] Ardenkjaer-Larsen, J. H. *et al. Proc. Natl. Acad. Sci.* **2003**, 100, 10158–10163
[2] Gajan, D. *et al., PNAS*, **2014**, 111, 14693-14697

Parallel DNP and EPR measurement at higher fields (6.7T and 18.8T) (P-2)

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Dynamic nuclear polarization (DNP) is a hyperpolarization technique that mediates polarization transfer from unpaired electrons to NMR-active nuclei via microwave irradiation. The characterization of the DNP polarizing agents using EPR provides useful information that helps understand the DNP mechanism. We are building a low-cost LOD EPR [1,2] circuit for EPR detection at low temperature (1.2K) DNP system. The basic working principle of the LOD EPR setup is that we will insert a coil parallel to the static magnetic field, to measure the induced current due to, the change in the longitudinal EPR magnetization upon amplitude or frequency of microwave or the magnetic field.

The EPR detection circuit consists of a copper coil aligned parallel to the static field. The circuit is non-resonant and well isolated from ground to minimize cross talk with the power-modulation signal. The coil is connected in differential mode to an audio preamplifier and followed my a low pass filter to block high frequency noise. The signal is then either fed into a data acquisition device (DAQ) for lock in detection in LabView or into a lock-in amplifier. We performed DNP and EPR at the same system at the same conditions to get an insight into the different DNP mechanisms.

References:
[1] Granwehr, Josef, Jörg Forrer, and Arthur Schweiger. "Longitudinally detected EPR: improvedinstrumentation and new pulse schemes."Journal of Magnetic Resonance151.1 (2001): 78-84
[2] Lê, T.P., Hyacinthe, J.N. and Capozzi, A., 2022. How to improve the efficiency of a traditional dissolution dynamic nuclear polarization (dDNP) apparatus: Design and performance of a fluid path compatible dDNP/LOD-ESR probe. *Journal of Magnetic Resonance*, *338*, p.107197.

Development of a Broadband On-Chip EPR Spectrometer (P-3)

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Conventional Electron Paramagnetic Resonance (EPR) spectrometers are limited by their narrow bandwidth and large physical dimensions. To overcome these limitations, we present a path towards a broadband on-chip EPR spectrometer. The broadband approach allows applications such as the distinction between field-dependent and field-independent processes like the Electron-Zeeman Interaction and Zero-Field Splitting. Moreover, an on-chip spectrometer can reduce size, cost, and complexity of the overall system. Such a device can be realized by using a broadband transmission line instead of a narrowband resonator-based coupling structure.

As a first step, we compare three different system architectures to realize the envisioned EPR spectrometer. All measurements are done at a frequency range from 0 to 28 GHz with a coupling structure based on a meandered co-planar transmission line. The first architecture is a superheterodyne receiver where the EPR signal is measured on a fixed intermediate frequency. The second architecture extends this with an interferometer to cancel the unwanted large signal so that only the small EPR signal is present on the receiver. The third architecture is a millimeter-wave detector with lock-in detection.

For a first implementation of an on-chip EPR spectrometer, the third architecture is chosen because it has the lowest requirements for the millimeter-wave components and has a high signal-to-noise ratio due to the inherently good filter capabilities of the lock-in principle. Two components central to the prototype, a single-ended broadband amplifier and a corresponding detector, were designed and manufactured. The characterization of the two integrated circuit components is presented.

Influence of methyl and ethyl rotors on electron spin decoherence (P-4)

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The low-temperature Hahn echo decay/two-pulse electron spin echo envelope modulation (ESEEM) signal contains two contributions on different time scales. The slower contribution arises from nuclear pair ESEEM,[1] whereas methyl tunneling causes ESEEM on a faster time scale.[2] The methyl quantum rotor (MQR) model describes the overall signal in terms of multiple methyl rotors coupled to an electron spin and accounts for different local environments in a glassy matrix using a rotation barrier distribution.[3] Tunneling ESEEM strongly depends on the matching of the difference in hyperfine couplings of the methyl protons with the tunneling frequency.[4] Methyl rotors beyond geminal methyl substituents in nitroxides and CH_3-groups present in vanadium(IV) complexes' counter ions influence the spin systems' decoherence behavior.[5]

Here, we compare rotation barrier distributions from various nitroxides with geminal methyl and ethyl substituents and explain the differences in their two-pulse ESEEM signals using the MQR theory. Moreover, we investigate "mixed" nitroxides containing different types of methyl rotors and rationalize their electron spin decoherence.

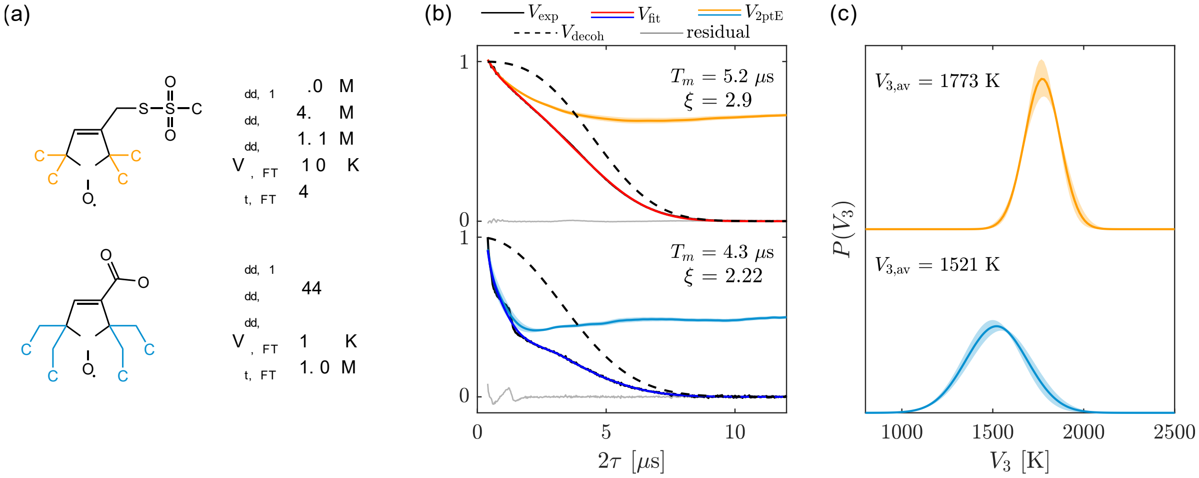

***Figure 1**: (a) Structures of MTSL (top) and gem-diethyl-nitroxide (bottom) with hyperfine couplings ν_{dd} and DFT-calculated rotation barriers V_3. (b) Hahn echo decay fits of MTSL (orange) and gem-diethyl-NO (blue) measured at 20 K at Q-band using the MQR model and (c) their corresponding Gaussian rotation barrier distributions.*

[1] G. Jeschke, *JMRO* **2023**, *14-15*, 100094
[2] S. Soetbeer et al., *PCCP* **2021**, *23*, 21664-21676
[3] A. Eggeling et al., *submitted*
[4] M. Šimėnas et al., *Sci. Adv.* **2020**, *6*, eaba1517
[5] Jackson et al., *J. Phys. Chem. C* **2022**, *126 (16)*, 7169-7176

Need for speed: Rapid-scan electron paramagnetic resonance (P-5)

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Background: Rapid-scan electron paramagnetic resonance spectroscopy in combination with site-directed spin labeling is an emerging technique which substantially improves the signal-to-noise ratio and time resolution compared to conventional continuous-wave experiments. Rapid-scan signals are directly recorded without the use of phase-sensitive detection. The main magnetic field is centered at resonance, the microwave power is constant, and an additional set of coils is used to scan through the spectrum thousands of times per second. Since the time on resonance is short compared to relaxation times, higher microwave powers can be applied which consequently shortens the time required to accumulate the spectrum.

Rapid-scan is thus well suited for studying fast biochemical kinetics accompanied by spectral changes of the EPR lineshape.

Purpose: Rapid-scan provides numerous of possible applications to investigate the structure and dynamics of a variety of samples in material science, chemistry and biology. Particular interest is put to implement rapid-scan for clinical usage such as in EPR dosimetry, oximetry or the study of Alzheimer’s and Parkinson’s disease. Recent developments clearly highlight the potential of this new spectroscopic method while pointing out opportunities to revolutionize the way in which EPR is done in the future.

Methods: Rapid-scan signals require extensive post-processing methods to be applied before interpretation. The actual EPR spectrum, for instance, is superimposed by a strong background that is caused by microphonic effects of the rapidly changing magnetic field.

Results:
- A novel procedure was recently developed that allows to eliminate the background while exploiting the full potential of combining the up-and downfield scan for an increased signal-to-noise ratio (currently revised to be published in Journal of Magnetic Resonance – Frontiers of EPR)
- First time resolved rapid-scan experiments have been conducted to investigate the early stages of Alzheimer’s disease

Future prospects: Mapping electrostatics and local pH-values of proteins are upcoming projects to be addressed soon.

Strategies for Frequency and Time Domain Simulations of Pulsed ENDOR Experiments (P-6)

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ENDOR spectroscopy is a tool to study nuclei interacting with electrons. To derive detailed structural information from experiments careful analysis and simulation is crucial.

The most widespread approach are *frequency-domain* simulations: ENDOR resonance frequencies are calculated from the spin Hamiltonian and simulated as a ‘stic ’-spectrum. This is convoluted with a line-shape function containing line broadening and possible effects of the pulse sequence. The approach is relatively fast and easily accessible and we expanded it by implementing a statistical analysis of the experimental spectrum through application of a ‘drift-model’[1] and introducing Bayesian optimization for the simulation parameters. Together with bootstrapping parameter uncertainties can be determined. The ‘analysis-pipeline’ from the experimental data to derived structural parameters will be presented here.

Time-domain simulations directly calculate the effect of the pulses on the spin-density matrix over the whole time evolution of the experiment.[2] This allows to evaluate and understand the spin-dynamics in advanced pulse ENDOR sequences, e.g. cross-polarization ENDOR.[3] In the simulation different physical aspects can be considered, e.g. the anisotropy B-term of the hyperfine coupling or T_2-relaxation. These effects can then be assigned to effects detected experimentally. Thereby, the potential strengths and weaknesses of pulse sequences can be assessed without the necessity of intensive optimization and comparisons in practice.

References:
[1] Y. Pokern et al, *PNAS*, **2021**, *118*, e2023615118
[2] I. Bejenke, et al., *Mol.Phys.* **2020**, *118*, e1763490
[3] R. Rizzato, et al., *Mol.Phys.*, **2013**, *111*, 2809-2823

Set-up of a Novel Very High Frequency EPR Spectrometer for Sensitive Broadband Detection of Transition Metal Ion Complexes (P-7)

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We present the design and set-up of a novel very high frequency EPR spectrometer (HFEPR) for sensitive broadband detection of paramagnetic metal centres, transition metal ion (TMI) complexes and iron based catalysts. Operating in the terahertz range at multiple frequencies (80, 160, 240, 320, 480 and 960 GHz), it overcomes conventional EPR limitations such as restricted frequency range, limited resolution and challenges in accurate determination of zero-field splitting (ZFS).

Our strategy to overcome these limitations involves utilizing high-field/high-frequency techniques, state-of-the-art quasi-optical components and ultra-sensitive induction mode detection. Innovations in our spectrometer design include employing multi-frequency sources together with a unique multimodal corrugated waveguide produced to optimally transmit radiation across the entire 80-1100 GHz bandwidth. This approach enhances sensitivity and expands the accessible frequency range.

The spectrometer incorporates a cryogen-free 12 T magnet, bolometer detector and high power multiplier chain. It supports frequency/field sweeps: 10% of carrier frequency and 0-12 T, with sample holders compatible with both pressed pellets and X-band EPR tubes. The target concentration sensitivity is in the 10 μM range for high spin states.

Herein, we focus on providing solutions to optimize high-field equipment, tackling insertion losses of individual microwave components and frequency-dependent transmission properties. We tested the quasi-optical microwave bridge (by TKLtd) performance across multiple frequencies evaluating transmission properties and emission channels isolation crucial for spectrometer sensitivity. Our findings demonstrate the potential of this innovative HFEPR spectrometer for measuring TMI complexes with large ZFS not only in polycrystalline form, but also in frozen liquid solution.

Exploring Spin Dynamics during Electron Spinlock Pulses (P-8)

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Long microwave (MW) pulses are part of numerous pulsed EPR experiments including ELDOR detected NMR and cross-polarization ENDOR. Moreover, they can be used to lock transverse magnetization along the MW magnetic field in what is called a spinlock pulse. Under these conditions, spins are in the dressed state [1], which has possible advantages such as slower transverse relaxation.

However, understanding the spin dynamics during spinlocking is non-trivial because relaxation under MW irradiation plays a crucial, yet not fully understood role. Here, we use a commercial Bruker E680 W-band (94 GHz) EPR-spectrometer in combination with a SpinJet arbitrary waveform generator to analyse the effect of long MW pulses and the behaviour of dressed spins.

Chirp echo EPR spectroscopy (CHEESY, fig. a) allows us to analyse inversion and excitation profiles of spinlock pulses [2] and ultimately, to observe the transition from a pulse with well-defined rotation properties to a spinlock or high turning angle pulse. Using phase modulation schemes, dressed state pulse sequences like dressed spin echoes are implemented [3] (fig. b). The results suggest that spinlock under high-field EPR conditions achieves selective locking of resonant spins and show an increase of transverse relaxation time in the dressed state. Furthermore, we demonstrate the interchangeability of dressed and free state pulse sequence elements using modified dressed experiments (fig. c).

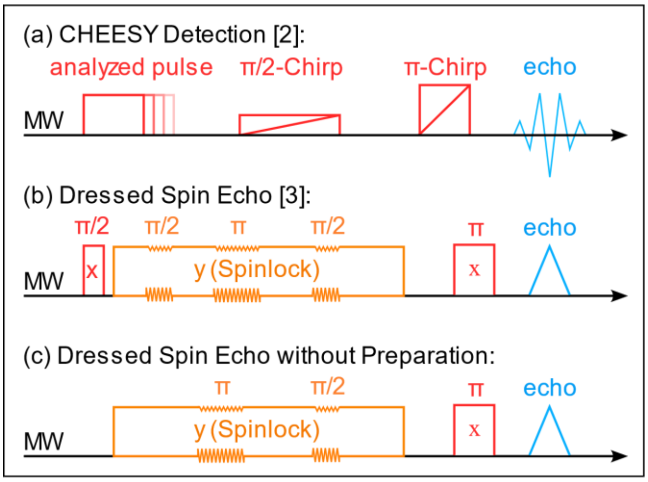

***Figure 1**: Pulse sequences for Chirp echo detection (a) and dressed spin experiments (b,c).*

References:
[1] G. Jeschke, *Chemical Physics Letters* **1999**, *301*, 524-530
[2] N. Wili et al., *Journal of Magnetic Resonance* **2018**, 289, 26-34
[3] N. WIli et al., *Magnetic Resonance* **2020**, *1*, 75-87

Comparison between Gd(III) complexes for DEER measurements (P-9)

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For DEER measurements Gd(III) complexes present a higher stability within biological cells and an improvement of sensitivity due to their high spin properties compared to nitroxides.[1][2] They also provide a paramagnetic centre with complementary EPR spectral properties to nitroxides.

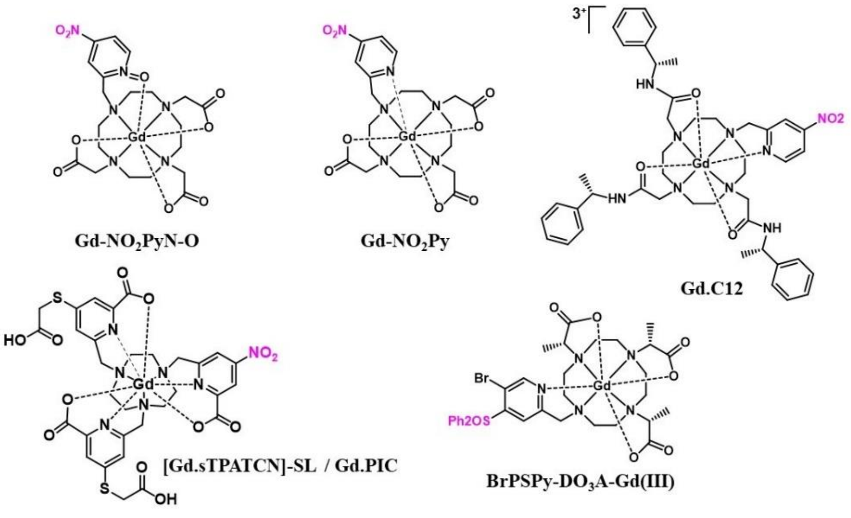

***Figure 1**:* The structure of the four Gd(III) complexes compared, and BrPSPy- O A-Gd(III) the preferred spin label at the moment for *in cell* measurements.

In this study, we took a Calmodulin-M13 peptide construct with two cysteine residues and tested the spin labels shown in Figure 1 for reactivity and their comparative distance distribution results from DEER. The DEER measurements were taken at W-band at the Weizmann Institute, Israel and with HiPER in St Andrews

References:

[1] Shah A., et al., (2019), A Gadolinium Spin Label with Both a Narrow Central Transition and Short Tether for Use in Double Electron Electron Resonance Distance measurements, Inorg. Chem., 58, 3015-3025.

[2] Giannoulis A., et al., (2021), Chapter Eight – Characteristics of Gd(III) spin labels for the study of protein conformations, Methods in Enzymology, 651, 235-290.

The Design and Construction of a 13.8 T EPR Spectrometer for the Investigation of Dynamic Nuclear Polarization Mechanisms (P-10)

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Dynamic Nuclear Polarization (DNP) has been shown to enhance Nuclear Magnetic Resonance (NMR) signals by orders of magnitude, thus vastly expanding the range of NMR applications. To maximize the benefits of DNP, the experiments must be performed at high magnetic fields typical for modern NMR experiments.

A detailed understanding of quantum mechanical DNP mechanisms is essential for our ability to design improved DNP experiments and polarization agents. This understanding necessitates knowledge about the electron spin dynamics, available only through Electron Paramagnetic Resonance (EPR) measurements. Experiments at low magnetic fields, where commercial EPR instruments are readily available, and at 3-7 T using dedicated home-built DNP/EPR instruments provided a wealth of information on DNP mechanisms [1]-[3]. At higher magnetic fields DNP experiments were limited to nuclear detection, and our understanding of electron spin dynamics stems from simulations, in the absence of experimental measurements, due to the unavailability of very high field DNP/EPR spectrometers.

During the past four years, a dual DNP / EPR instrument operating at ~14 T was constructed in our laboratory at Tel-Aviv University. The spectrometer is capable of CW and pulsed, including pulse shaping, EPR and multinuclear DNP experiments. In this presentation, we present the instrument’s design and its current state.

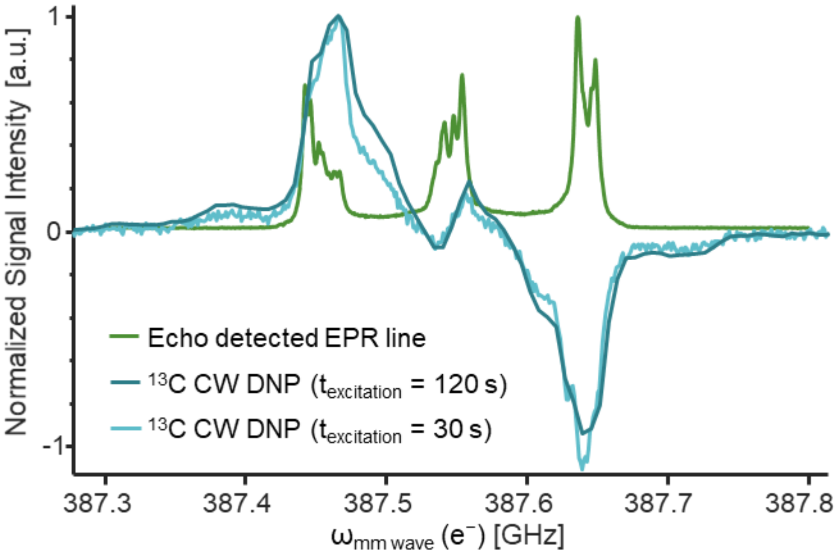

Figure 1: *^{13}C CW DNP sweep and echo detected EPR spectra of P1 centers in diamond at 13.8 T and RT.*

References:
[1] A. Feintuch et al., *J Magn Reson* **2011**, *209*, 136-141
[2] Y. Hovav et al., *Phys. Chem. Chem. Phys* **2014**, *17*, 226-224
[3] T. A. Siaw et al., *J Magn Reson* **2016**, *264*, 131–153

A unified description for polarization-transfer mechanisms in magnetic resonance in static solids: Cross polarization and DNP (P-11)

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Polarization transfers are crucial building blocks in magnetic resonance experiments, i.e., they can be used to polarize insensitive nuclei and correlate nuclear spins in multidimensional nuclear magnetic resonance (NMR) spectroscopy. The polarization can be transferred either across different nuclear spin species or from electron spins to the relatively low-polarized nuclear spins. The former route occurring in solid-state NMR can be performed via cross polarization (CP), while the latter route is known as dynamic nuclear polarization (DNP). Despite having different operating conditions, we opinionate that both mechanisms are theoretically similar processes in ideal conditions, i.e., the electron is merely another spin-1/2 particle with a much higher gyromagnetic ratio. Here, we show that the CP and DNP processes can be described using a unified theory based on average Hamiltonian theory combined with fictitious operators. The intuitive and unified approach has allowed new insights into the cross-effect DNP mechanism, leading to better design of DNP polarizing agents and extending the applications beyond just hyperpolarization. We explore the possibility of exploiting theoretically predicted DNP transients for electron–nucleus distance measurements—such as routine dipolar-recoupling experiments in solid-state NMR

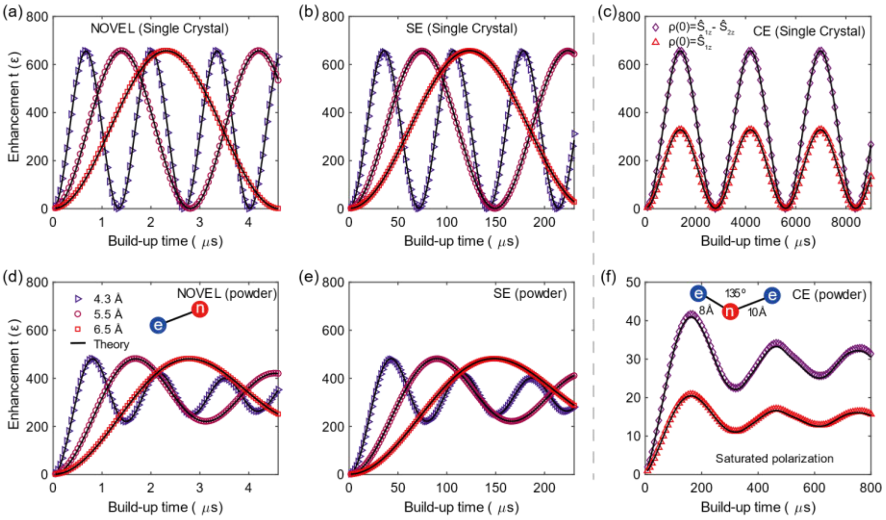

***Figure 1**: Plots of ^{1}H enhancement calculated by theory (line) and numerical simulations for (a, d) NOVEL, (b, e) SE, and (c, f) CE on (a-c) single-crystal or (d-f) powdered samples.*

Control of excitation selectivity in spin-correlated radical pairs with shaped pulses (P-12)

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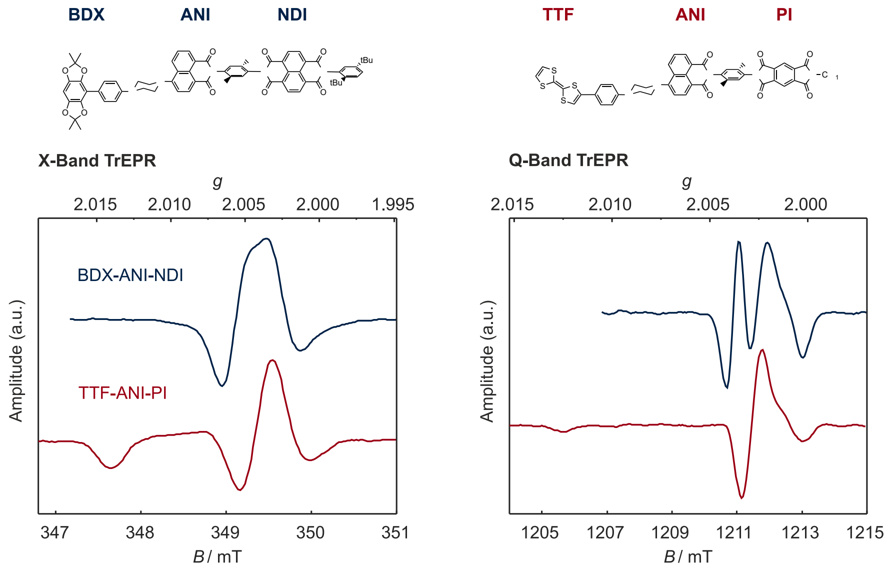
Spin-Correlated Radical Pairs (SCRPs) formed by photoinduced electron transfer play a fundamental role in a wide range of photochemical and biochemical processes and, on account of their unique properties, are also of interest for potential applications in quantum information technology and spintronics.[1] SCRPs are characterized by a unique spin polarization and an unusual behaviour in pulse EPR experiments with non-selective excitation.[2,3] The advent of pulse shaping in EPR provides the opportunity for increased control over excitation selectivity for pulse EPR on SCRPs, with important consequences for the characterization of SCRPs and their use in quantum information science.

We have investigated two singlet-born photogenerated SCRPs with different spectral widths[4,5] (Figure 1) by means of pulse EPR with both selective and non-selective shaped pulses to further unravel the unusual behaviour of SCRPs and to determine if shaped pulses can provide better results compared to standard rectangular pulses. Our investigations lay the foundation for optimum-control-based approaches to pulse EPR on these species.



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Design and Characterization of novel Microresonators for HF-EPR Spectroscopy (P-13)

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With the progressive research in quantum technologies Electron Paramagnetic Resonance (EPR) spectroscopy is becoming increasingly attractive as a read-out method for quantum states on thin films. Especially EPR spectrometers operating at high frequencies (HF) are getting increasing attention, due to their higher sensitivity, resolution and access of usually EPR-silent molecules. A common problem for HF-EPR is the insufficiency of cavity resonators in the THz regime, making the development of novel resonator types necessary. In this project microresonators for thin film measurements are designed and optically characterized, which use the interplay of the Fabry-Pérot effect and an array of plasmonic metasurface antennas to enhance the magnetic field of the incident microwave. More spin transitions take place, resulting in an increased signal and better signal-to-noise ratio. The introduction of a novel antenna arrangement into rows leads to the emergence of lattice modes, promising a stronger magnetic field enhancement, better quality factors and controllable resonance frequencies.

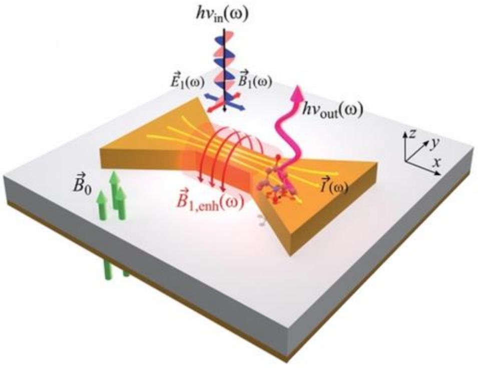

***Figure 1**: Overview of the working principle of plasmonic metasurface antennas. The antennas' electrons are excited by the electric field component (E_1) of the incident THz radiation and leads to an electron oscillation along the antennas' bridge. This current I induces a magnetic field ($B_{1,enh}$) around the bridge, strengthening the magnetic field (B_1) of the THz radiation [1].*

References:
[1] L. Tesi et al., *Small Methods*, **2021**, *5*, 2100376

autoDEER – Spectrometer-Independent Pushbutton DEER (P-14)

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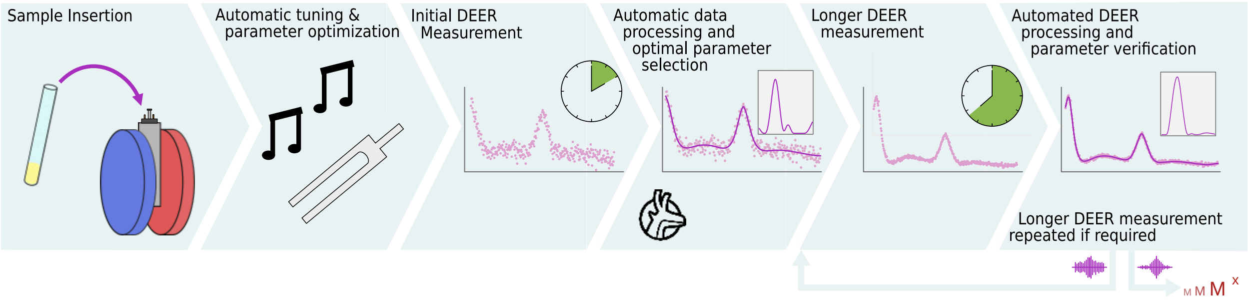
An important step in both improving the reproducibility and the reliability of distance measurements in Double Electron Electron Resonance (DEER) spectroscopy is the development of a fully automated procedure. Such a procedure could also reduce the entry barrier to non-experienced users and reduce the potential for human bias.

Here we present autoDEER, a Python package for conducting push-button automatic DEER measurements on both commercial Bruker and homebuilt spectrometers.

Key features included in autoDEER:

- **Fully automated control:** A fully automated push-button mode controls the entire spectrometer including setup, allowing the user to walk away. There is also an advanced mode, allowing the user to write their own automation scripts or precisely control the measurement.
- **Support for a variety of DEER variants:** When run in push-button mode, the software will select an optimal DEER sequence for the user's specific sample and conditions. However, when using the advanced mode, the user can select from a wide range of DEER variants, such as four-pulse, five-pulse, seven-pulse DEER and nDEER.
- **Integrated analysis:** Both during and after a DEER measurement, the software actively processes and analyses the data using DeerLab[1]. Allowing for continuous verification of sequence parameters, and distance distribution convergence.
- **Parameter optimisation:** Sequence parameters are determined and optimised from the integrated analysis. This includes inter-pulse delays, pulse excitation bands, and pulse amplitudes.
- **Hardware independence:** This toolbox is spectrometer independent and supports both modern Bruker Elexsys-II (using the XeprAPI) and home-built spectrometers.

More information can be found at: jeschkelab.github.io/autoDEER



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Design of a new spin probe: A water soluble N@C60 (P-15)

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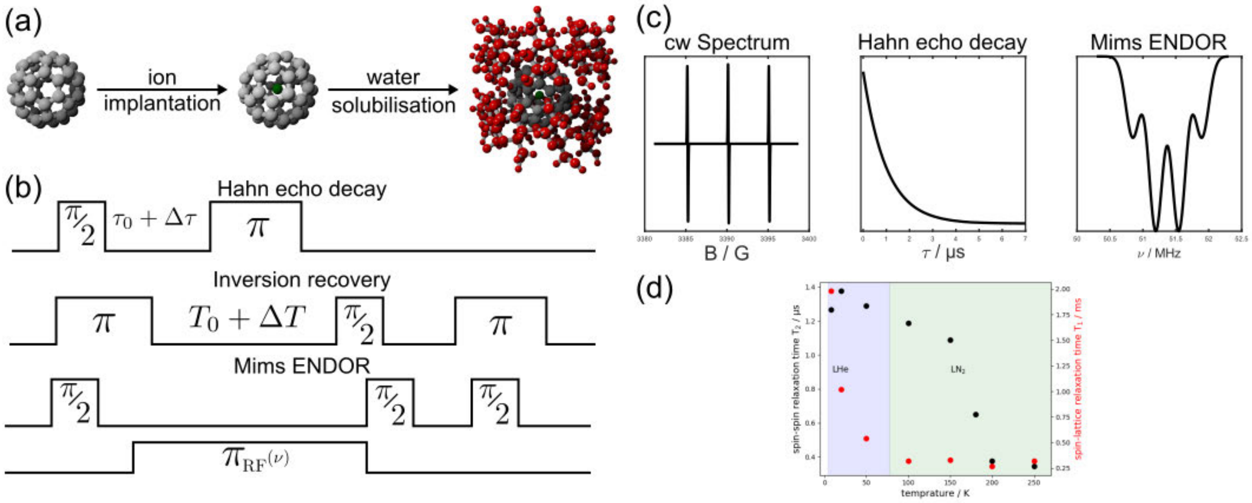
A spin-based study of a guest-host complex consisting of an endohedral fullerene ($N@C_{60}$) and γ-cyclodextrin (GCD) is performed [1]. $N@C_{60}$ stands out with its excellent properties according to spin relaxation times and its chemical stability. The sample preparation is based on ion bombardment [2] and encapsulation into the GCD succeeds *via* a grinding method [3]. Via cw EPR it can be shown that the spin properties of $N@C_{60}$ are largely conserved by the narrow linewidth at room temperature. Pulsed EPR techniques provided information about the relaxation times, which show a temperature dependent sweetspot in the liquid nitrogen regime. Furthermore, Mims ENDOR experiments [4] were performed and compared with molecular dynamic simulations to gain further insights into the chemical structure of the 1:2 $N@C_{60}$:GCD complex.



***Information about $N@C_{60}$:GCD complex**: (a) Overview of fabrication process (b) Pulse sequences for standard experiments (c) From left to right: X-band cw EPR spectrum, Hahn echo decay and Mims ENDOR spectrum from $N@C_{60}$:GCD (d) Temperature dependence of the relaxation times of $N@C_{60}$:GCD*

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A Simulation-Independent ESR Spectral Analysis Approach Using Wavelet Transform (P-16)

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Accurate analysis of continuous-wave electron spin resonance (cw ESR) spectra of biological or organic free-radicals and paramagnetic metal complexes is key to understand their structure-function relationships and electrochemical properties. However, in the presence of *g*- and/or *A*-anisotropy and/or large number of hyperfine lines, spectral analysis becomes highly challenging. Either high-resolution experimental techniques are employed to resolve the spectra in those cases or a range of suitable ESR frequencies are used in combination with simulations to identify the corresponding *g* and *A* values. Simulation-based analysis often fails to extract spectral information fully and accurately from non-ideal spectra. In addition, such analyses are highly sensitive to spectral resolution and artifacts, users' defined input parameters and spectral complexity. We introduce a simulation-independent wavelet packet transform-based analysis which extract *g* values and hyperfine (*A*) constants directly from cw ESR spectra, enabling broader application of ESR. Our method overcomes the challenges associated with simulation-based methods for analyzing poorly / partially resolved and unresolved spectra, which is common in most cases. The accuracy and consistency of the method are demonstrated on a series of experimental spectra of organic radicals and copper-nitrogen complexes. We showed that for a two-component system, the method identifies their individual spectral features even at a relative concentration of 5% for the minor component.

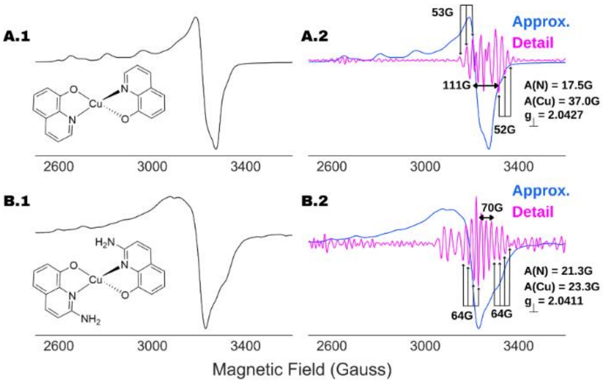

***Figure 1**:* Recovery of nitrogen-hyperfine structure and coordination of Cu(**II**) center in (A) CuQu and (B) CuQuA.

References:

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Relaxation rates from ENDOR variants: Potential and Limitations (P-17)

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Relaxation rates of nuclear spins in the close vicinity of a paramagnetic metal center harbour information on electronic structure that is currently largely unused. These relaxation rates influence spectra obtained by the Davies electron-nuclear double resonance (ENDOR) experiment (Fig. a). At low temperatures and high frequencies (Q-band and higher) line asymmetries may appear in the spectrum (Fig. c) that depend on the electron, nuclear and cross relaxation rates (Fig. b) as well as on the interpulse delays and the hyperfine coupling sign. [1]

In this project, we evaluate these line asymmetries in ENDOR spectra to investigate the relaxation behaviour of nuclear spins near the paramagnetic centre in copper and titanium model systems. In this pursuit, we test multiple ENDOR variants (Variable (Pre-)Mixing Time ENDOR, Saturation Pulse ENDOR) to access electron-nuclear cross relaxation rates. We fit data based on a theoretical description that includes the relaxation behaviour during the evolution periods of the ENDOR variants as well as inversion recovery and Hahn echo saturation experiments. Thereby, we assess the performance of the various techniques for disentangling the relaxation rates and identify the current limits of the techniques.

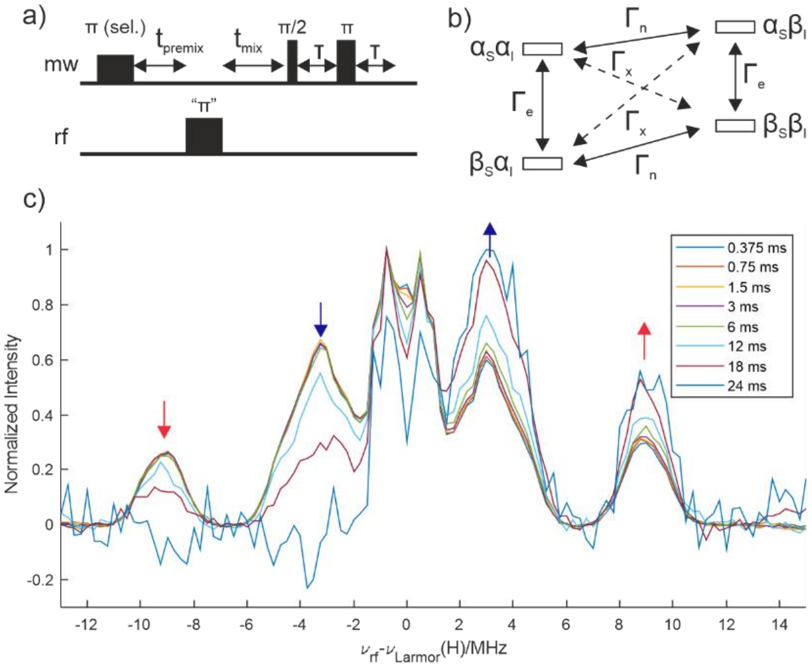

***Figure 1**: a) Davies ENDOR pulse sequence b) Relaxation pathways of an idealized 2-spin system c) ENDOR spectrum of model protein ScoI-Cu^{2+} for several mixing times (12 K).*

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High volume continuous flow DNP resonators (P-18)

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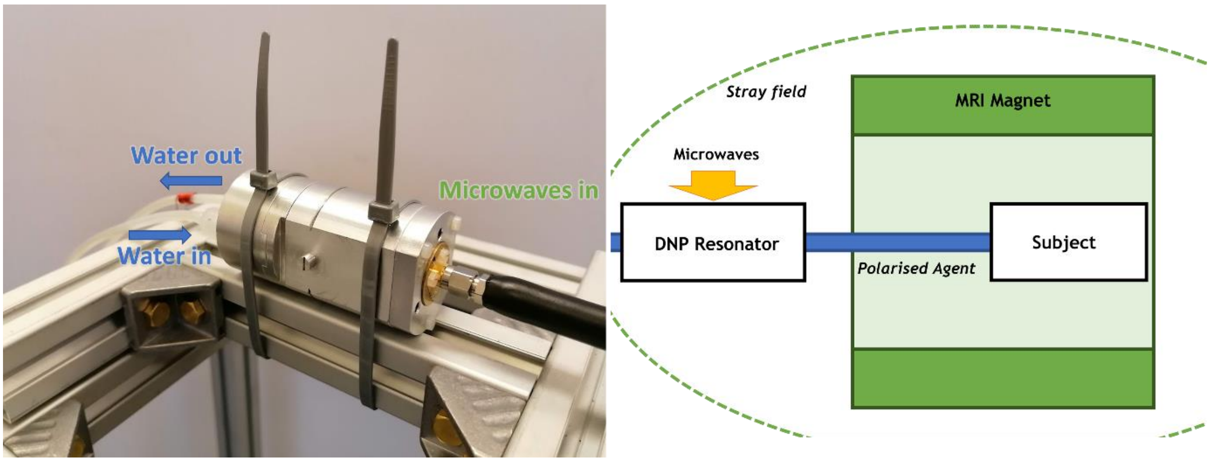

Figure 1. *Left; high volume continuous flow DNP resonator prototype. Right; illustration of intended continuous flow DNP MRI system.*

Dynamic nuclear polarisation (DNP) is a hyperpolarisation technique which can drastically increase the signal to noise ratio of nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) measurements by many orders of magnitude. Over the last two decades, various attempts have been made to produce a continuous flow of DNP enhanced fluids. More recently, these efforts are motivated by the need for alternative contrast agents for MRI[1] and the desire for improved sensitivity for liquid state NMR[2].

Thus far, continuous flow DNP systems have had limited applicability to medical MRI due to their relatively low volume flow rates, limited by cavity losses and small sample volumes. This project aims to design a continuous flow DNP system (fig. 1), capable of polarising at flow rates 10 times greater than those previously reported in literature. Extensive electromagnetic modelling has been carried out to develop and optimise new resonator designs, followed by several prototype stages. Effort has been made to reduce dielectric losses, in order to polarise large sample volumes. Modelling suggests that high polarisation is achievable at flow rates of 30 mL/min, which has been identified as a target for medical DNP MRI.

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Optimizing AWG-pulses for broadband excitation (P-19)

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In pulsed EPR, conventional rectangular pulses are not able to fully excite the widths of typical EPR spectra.

Specifically for nitroxides, which are the most common spin label used in EPR, the available microwave power is usually not sufficient, even at X-Band frequencies. This limits not only the sensitivity but also the type of experiments that can be performed efficiently.

With the introduction of arbitrary waveform generators (AWGs) to EPR, phase and amplitude modulated pulses have made it possible to achieve higher excitation bandwidths.[1,2,3]

In this poster I will compare frequency-swept pulses as well as optimum-control theory (OCT) pulses to conventional rectangular pulses and discuss their implementation into the EPR setup.

Frequency-swept pulses have the advantage that they are fairly easy to implement and that they can, with some adaptions, be introduced to most known pulse sequences in EPR. On the other hand, they introduce offset dependent phase shifts which need to be addressed by additional compensation schemes.

OCT pulses can in principle achieve homogeneous phase over a specified bandwidth while also taking in to account fluctuations in the pulse amplitude and other imperfections.

But for both pulse categories, it is important to characterize and compensate distortions by the spectrometer for a given combination of sample and resonator coupling, to be able to successfully implement them.

References:

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Straightforward Background Correction in Dipolar Spectroscopy (P-20)

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Pulsed dipolar electron spin resonance spectroscopy (PDS) is a powerful tool in structural biology, particularly to study disordered systems and their transition to ordered states. PDS can obtain the probability distribution of distances between a pair of spin labels, *P(r)*, whose shape can offer information about whether a defined distance, multiple distances, or a broad ensemble of distances are populated. The *P(r)* is encoded by a time domain signal, *V(t)*, that contains a sum of the dominant oscillation of intramolecular interactions combined with monotonous decay from the average of oscillations of intermolecular interactions referred to as background signal. Two approaches are commonly utilized to treat the background: one-step analysis to simultaneously fit the background and *P(r)*; and two-step analysis, where the background is fitted on a *V(t)* and removed by either subtraction or division. The background is easy to remove for systems with defined intramolecular distances; however, disordered systems contain broad or multi-distances, while having unknown spatial dimensions. Even though the approximate background can be extracted from fitting the signal of a single-labelled sample of similar composition, it is still difficult to properly select the part of the *V(t)* with only intermolecular contributions, while having to perform additional experiments. We present a background correction method utilizing wavelet transform to accurately select the intermolecular contribution, fit the contribution, and then remove it by subtraction in the logarithmic domain. We demonstrate this method on simulated *V(t)* and experimental *V(t)* of the intrinsically disordered protein, tau, and its fibrillar state.

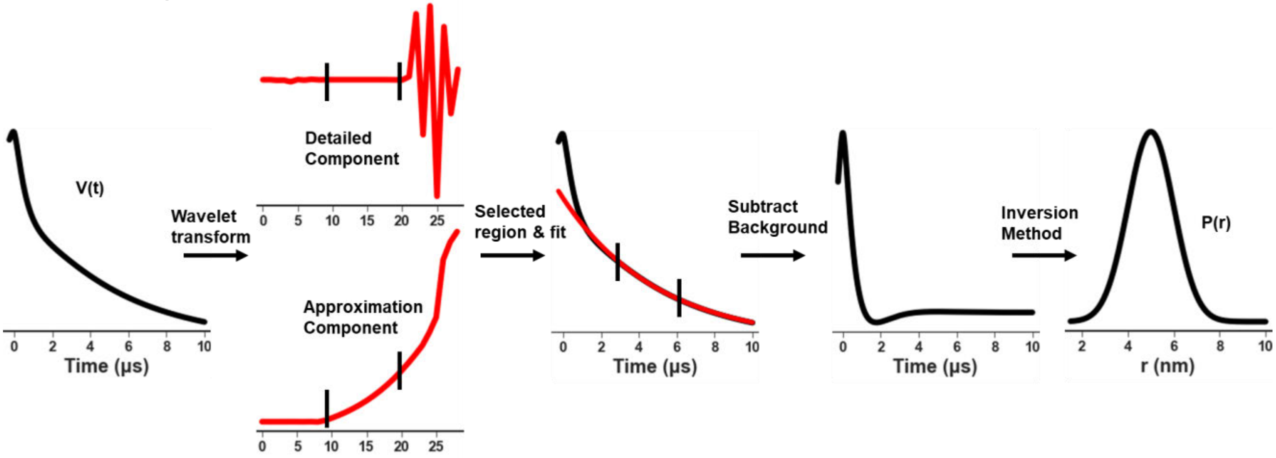

Figure: *Background Correction Process*

Single electron-spin-resonance detection by microwave photon counting (P-21)

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We report a new method for the detection of single electron spins at millikelvin temperatures. Analogous to the optical fluorescence detection of atoms or molecules, it consists in detecting the microwave photons spontaneously emitted by an electron spin when it relaxes radiatively to its equilibrium ground state after being excited by a pulse. The method applies to all paramagnetic species with sufficiently low non-radiative decay rate; here, we demonstrate it on rare-earth-ion spins (Er^{3+}) doped in a $CaWO_4$ host matrix using a microwave photon counter at cryogenic temperatures. We resolve individual narrow peaks in the fluorescence signal, on which we observe microwave photon anti-bunching, proving that they originate from single spins. We reach a signal-to-noise ratio of 1 in 1 second integration time for each Er^{3+} ion. We observe spin coherence times above a millisecond, limited by the radiative lifetime.

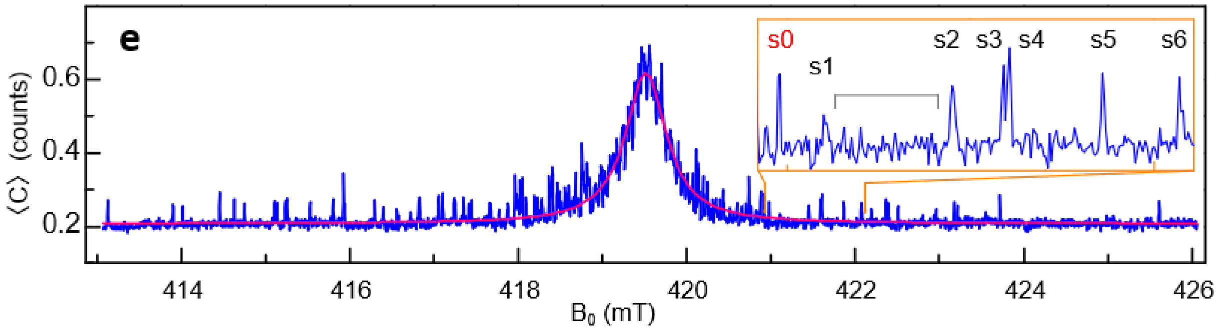

***Figure 1**: Spin spectroscopy at low power Blue line is measured data, red line is a Lorentzian fit. The inset shows an expanded view of 7 peaks corresponding to single electron Er^{3+} spins.*

References:
[1] E. Albertinale et al., Nature 600, 434 **(2021)**
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[3] R. Lescanne et al., Phys. Rev. X 10, 021038 **(2020)**
[4] Z. Wang et al., in preparation **(2022)**

Investigation of exchange- and dipolar interaction in highly conjugated Trityl biradicals (P-22)

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Normally, organic radicals are rather unstable and very reactive species. However, examples such as Nitroxide or Trityl radicals show that such species can be sufficiently stabilized. Especially Trityl radicals are known for their high chemical stability, both under reductive and oxidative conditions, their narrow EPR signals, and long relevant coherence times. Hence, they are used for applications such as spin labels for EPR based distance determination, magnetic resonance imaging, or dynamic nuclear polarization. However, examples of chemically coupled multi-spin systems based on Trityl radicals are rather scarce.[1,2,3] This is why there are only a few examples of multi-radicals in the strong coupling limit. Particularly strongly coupled Trityl biradicals are characterized by a decreased stability towards oxygen, due to the population of a triplet state. Furthermore, the apparent hyperfine coupling of the Trityls' ^{13}C-satellites is halved in the strong coupling limit. In this work I present a series of different Trityl biradicals with increasing length of the molecular bridge and investigate their isotropic exchange and dipolar interaction by means of cw- and pulsed-EPR and evaluate their influence on the spectra. The determination of the spin-spin interaction for a library of different molecular bridges will establish a toolbox for the design of new magnetic materials.

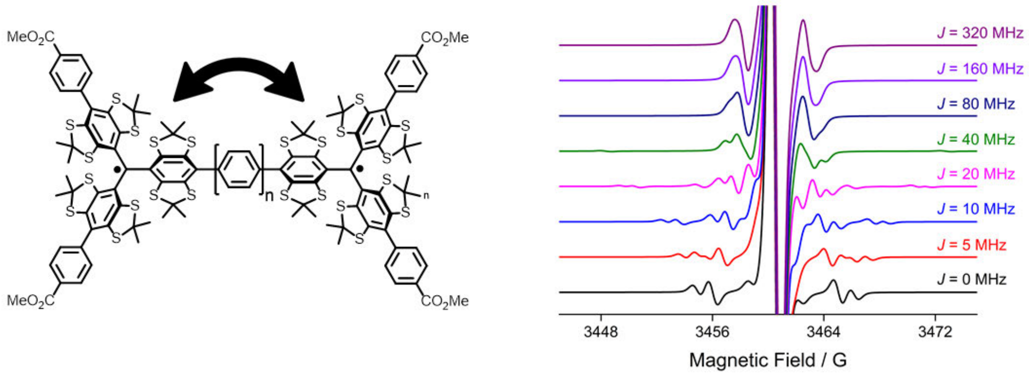

***Figure 1**: General Structure of Trityl biradicals and the influence of exchange coupling on the EPR-spectrum in different coupling regimes*

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Hyperfine Spectral Diffusion in RIDME experiment for probing local nuclear environment. (P-23)

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Hyperfine spectral diffusion is one of mechanisms of observable decoherence that can be formulated for pulse EPR experiments. This effect arises when an electron spin experiences variable hyperfine coupling to the surrounding nuclear reservoir. There are several phenomena in spin dynamics that can lead to spectral diffusion, of which the most popular is the homonuclear flip-flop transition. The effect of the spectral diffusion depends both on the static and dynamic properties of the nuclear reservoir and thus can be exploited to probe and compare different nuclear (in particular, protonic) environments.

In this work, our recent results in quantification of longitudinal hyperfine spectral diffusion in Relaxation-Induced Dipolar Modulation Enhancement (RIDME) experiment will be discussed [1]. The developed theoretical model was tested on the measured RIDME data from TEMPO radical in water-glycerol glasses with various deuteration degree. After that, the technique was generalized for the case of stochastically-labelled barley (1→3),(1→4)-β-D-glucan dietary fibers where the protonic environment is characterized by a distribution of local proton densities. For these systems, this method reveals 3 types of spin-label localization on isolated chains and close to inter-chain net of contacts [2].

Overall, this hyperfine technique is promising both for studying fundamental dynamic properties of many-spin systems, making a connection with the DNP field, and for direct application to inhomogeneous and un-/semi-structured media such as spin-labelled polymers and proteins.

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Characterization of Mn(II) complexes by EPR spectroscopy (P-24)

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Background: Paramagnetic metal ions like Mn(II) are well-suited candidates for spin labels in EPR spectroscopy. Mn(II) possesses a half-filled outer shell and small ground state orbital momentum, resulting in long T_1 and T_2 times. Apart from that, it has broad EPR spectra spanning a range of $\sim 100 - 1000\ \mathrm{G}$ $(\sim 100\mathrm{MHz} - 1\mathrm{GHz})$, which makes Mn(II) suitable for double electron-electron resonance (DEER) measurements as observer and pump pulse do not overlap. Moreover, the zero-field splitting (ZFS) in Mn(II) complexes influences the appearance of the EPR spectrum as well as relaxation properties, all of which affect their performance in distance measurements [1].

Purpose: Previous publications show that metal ions like Gd(III) can be applied as spin label at high-field frequencies (corresponding to W-band). Apart from that, its sensitivity is enhanced compared to nitroxide labels operating in X-band [2]. To elucidate the use of metal ions in the low-field limit (corresponding to X-band), we investigated the relaxation properties of manganese(II) complexes as a function of their electronic structure in the X-band.

Methods: CW EPR measurements to determine the ZFS parameters, pulsed EPR measurements to determine T_1 and T_2 of various Mn(II) complexes. Ideally, T_1 is short and T_2 as long as possible to ensure short measurement time and long coherence of the system.

Results: Our characterization of different Mn(II) complexes indicates that an increase in the magnitude of the ZFS results in a decrease in T_1 and T_2.

Future prospects: Suitable complexes are planned to be used in pulsed dipolar spectroscopy experiments.

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Improvement of the coherence time (P-25)

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Molecular spin systems due to their quantum properties could benefit new technologies through the design of quantum bits (qubits). Due to the possibility of being in a coherent superposition state other than the 0 and 1 states, qubits can reduce processing speed exponentially and can solve problems that are unsolvable today.

Low spin molecules are interesting for use in quantum computing[1]. Iron metallocenes are low spin molecules, with considerable magnetic anisotropy, with relatively fast spin relaxation time due to the dipolar interactions. Increasing the coherence time is essential to meet DiVicenzo's requirements[2] if we want our molecule to act as a qubit. So a new strategy has been employed: the encapsulation of metallocenes in a diamagnetic host to decrease the dipolar interactions because the frequencies of the environment change caused the coherence time to be long. In this way, the encapsulation stabilizes the interaction between the iron metal centers showing long coherence times, which can be relaxed through different mechanisms due to the intrinsic anisotropy of the molecule by means of: Orbach, Raman, direct, local mode and quantum tunnelling.

In this work, the following metallocenes have been chosen as guests: bis(pentamethylcyclopentadienyl)iron tetrafluoroborate and ferrocenium hexaflourophosphate. As host we have selected the curcurbit[n]uril family, depending on the size of the metallocenes we have chosen either cucurbit[7]uril or cucurbit[8]uril, so that the guest can be encapsulated inside.

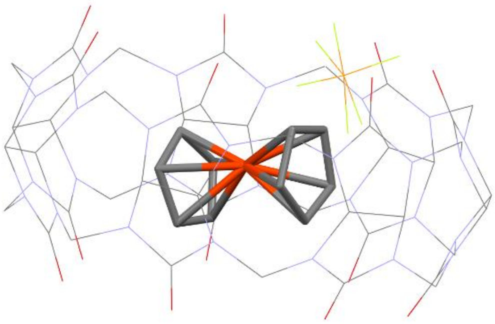

***Figure 1**: Encapsulation of ferrocenium in a curcurbit[7]uril.*

References:

[1] M.Atzori, R. Sessoli, J. Am. Chem. Soc. **2019**, 141, 11339-11352
[2] D.P. DiVicenzo, Fortschr. Phys. **2000**, 48 9-11, 771-783
[3] M. Amoza, et al. Chem. Eur. J. **2021**, 27, 16440-16447.

The surprising consequences of high electron polarization (P-26)

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The inherent low sensitivity of NMR can be overcome by hyperpolarization techniques, which increase the polarization of nuclear spins far beyond the Boltzmann equilibrium. One such method is dynamic nuclear polarization (DNP), which consists of transferring the high polarization of unpaired electron spins to surrounding nuclear spins *via* microwave irradiation. In the case of dissolution DNP (dDNP), the sample is hyperpolarized in the solid state at low temperature (1-2 K) and moderate magnetic field (3-7 T), where the Boltzmann polarization of electron spins approaches unity, translating into equally high nuclear polarization under DNP. In addition to yielding high nuclear polarization, the high electron polarization has other interesting consequences for NMR and EPR. Indeed, as the electron polarization tends towards unity, the electron flip-flop probability vanishes, an effect sometimes referred to as “bath quenching”. [1] By switching on and off microwave irradiation (microwave gating), one switches on and off electron flip-flops and hence paramagnetic relaxation. This has been shown to have a dramatic effect on transverse nuclear relaxation and on nuclear spin diffusion.[1-4] We present experiments where we used microwave gating to perform efficient CP, [2] to detect EPR properties indirectly *via* NMR properties, and finally to study nuclear spin diffusion in the vicinity of electron spins. [3,4]

References:

[1] Edwards et al., *JMR* **2012**, *223*, 198-206
[2] Bornet et al., *PCCP* **2015**, *18(44)*, 30530-5
[3] Stern et al., *Sci. Adv.*, **2021**, *7(8)*, eabf5735
[4] Chessari et al, *Arxiv*, **2022**, arXiv:2206.14771

Identifying non-lossy 3D printing materials for *in-situ* EPR cell fabrication (P-27)

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Quartz vessels are commonly used for EPR experiments because the low levels of paramagnetic impurities and high dielectric constant of quartz minimise its EPR signal without disrupting the resonator quality.[1] Unfortunately, constructing vessels from quartz is time-consuming and makes it difficult to incorporate additional features, thus limiting control over the vessel design. When designing new vessels for electrochemical-EPR, it is necessary to build many prototypes and to incorporate these additional features.

3D printing offers an alternative route, circumventing the limitations associated with quartz by enabling rapid prototyping and construction of more complex vessel designs. The two most common 3D printing technologies are fused deposition modelling (FDM) and stereolithography (SLA). A wide range of thermoplastics (for FDM) and photopolymer resins (for SLA) are commercially available, however very few have been tested and compared in terms of their EPR performance.[2,3] Here we present the first (to the authors’ knowledge) systematic study into the optimal printed materials for use in the EPR spectrometer cavity, searching for materials that have minimal signal and cause little disruption to the resonator quality, like quartz.

***Figure 1**: SLA-printed sample placed in the cavity of an EPR spectrometer.*

References:
[1] G. R. Eaton, S. S. Eaton, D. P. Barr and R. T. Weber, *Quantitative EPR*, Springer, New York City, 2010.
[2] A. Niemöller et al., *Journal of Magnetic Resonance*, **2016**, 269, 157–161.
[3] Y. Shi et al., *Journal of Magnetic Resonance*, **2019**, 308, 106593.

Single-Spin EPR Spectroscopy of a Metalloprotein (P-28)

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The sensitivity of commercial spectrometers is however limited, which makes EPR studies of micron-scale or low-concentrated samples difficult. Recently, a new detection method was demonstrated which reaches single-spin sensitivity [1]. The method, which requests cooling down the sample to millikelvin temperatures, relies on the enhancement of the spin radiative rate by coupling to a superconducting resonator, and on the detection of the emitted photon by a microwave photon counter based on superconducting circuits. In this doctoral project, the goal is to demonstrate the applicability of single-spin spectroscopy to spin systems of interest in EPR measurements, in particular metalloenzymes.

In that goal, suitable spin systems and deposition methods have to be identified and characterized. As a first system, we will use metmyoglobin that features a high-spin Fe(III) center, which can be converted to low-spin Fe(III) by a well-characterized reaction with azide. The metmyoglobin proteins will be embedded in a glassy matrix of trehalose.

The spin system shall be deposited on top of a planar superconducting resonator (see Figure) and characterized at the single-spin level.

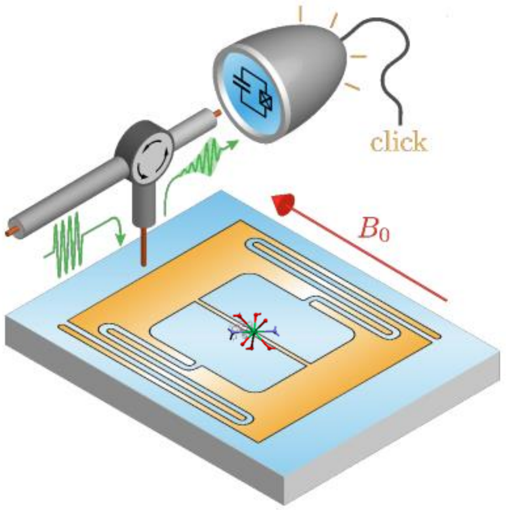

Figure 1: Schematic of the planned experiment. A metalloprotein is deposited on top of the inductance of a planar superconducting micro-resonator (in orange), with a magnetic field $B0$ applied to tune its frequency at resonance. The paramagnetic center Fe(III) is excited by a microwave pulse (green incoming arrow), and then relaxes by emitting a photon (green outgoing arrow), which is detected by a microwave photon counter based on a transmon qubit.

References:
[1] Z. Wang et al., arxiv:2301.02653, (to appear in Nature)

Materials and catalysis

Chemical tuning of trigonal lanthanide molecular qubits (P-29)

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One of the main advantages of molecular qubits is the ability to design derivatives of these, and thus tune the static and dynamic magnetic properties

Recently, vanadyl complexes were shown to behave as qubits even at room tempreture.[1] Lanthanide coordination complexes are much less studied, but offer enormous potential eg. it has been shown that Yb(trensal) displays coherence times of few 100´s of ns at 5 K and that its electron spin is coupled to its nuclear spin forming a coupled electronic qubit-nuclear qudit system.[2]

Very few studies exist, where systematic correlation between structure and coherence have been demostrated. We herein present derivates structurally simular to Ln(trensal), namely Ln(trenovan) and Ln(trenpvan) for whom methoxy groups have been attached to the trensal-scaffold. These systems crystalize in trigonal space groups, with the molecular C3 axis along the crystalografic c-axis. This allows for highly detailed investigations by C.W-EPR and other spectroscopic as well as thermodynamic techniques. Furtheremore we have investigated the dynamic magnetic properties by pulsed-EPR to examine how these small structural changes affect both the static and dynamic properties of these systems.

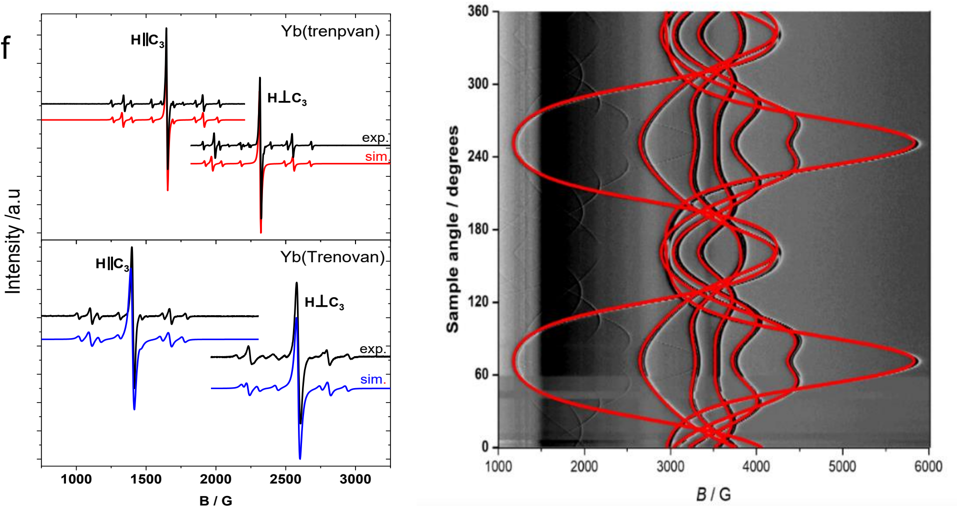

Figure 1*: LEFT: X-band C.W-EPR of single crystal of Yb(trenpvan)(top) and Yb(trenovan)(bottom) along and perpendicular to C$_3$ axis. RIGHT: X-band C.W-EPR rotation map of a single crystal of Gd(trenpvan) with simulation superimposed on top.*

[1] M. Atzori, R. Sessoli, Et al. (2016)Room- Temperature Quantum Coherence and Rabi Oscillations in Vanadyl Phthalocyanine: Toward Multifunctional Molecular Spin Qubits J. Am. Chem. Soc. 138, 7, 2154–2157.

[2] R. Hussain, S. Carretta, et al. (2018) Coherent Manipulation of a Molecular Ln-Based Nuclear Qudit Coupled to an Electron Qubit, J. Am. Chem. Soc. 140, 31, 9814–9818

Enabling Electrical Readout of Molecular Qubits (P-30)

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Organic semiconductors offer a promising platform for studying spin transport due to their weak spin-orbit and hyperfine interactions, resulting in longer spin lifetimes compared with most inorganic semiconductors [1]. Molecular quantum bits (MQBs), which are based on unpaired electron spins in molecules, show great potential for various quantum technologies due to their relatively longer spin lifetimes even at higher temperatures compared to other types of qubits [2]. Here, we investigate a model system consisting of a semiconducting polymer and an MQB as a novel platform for enabling an electrical readout of the qubit. We aim to detect a change in the spin state of the qubit by observing a change in the current through the system because of the spin-dependent interaction between the qubits and the charge carriers of the polymer.

We chose the polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT) due to its high charge carrier mobility, and the molecule molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] [Mo(tfd-CO_2Me)$_3$] because of its potential as both an MQB and a dopant for the polymer. We performed organic field-effect transistor (OFET) measurements on the polymer film and, pulsed electron paramagnetic resonance (p-EPR) spectroscopy on the qubit to characterize the conductivity and coherence times of the semiconductor and the qubit, respectively. Our next step is to investigate conductivity and spin coherence in the hybrid system using thin films of PBTTT doped with [Mo(tfd-CO_2Me)$_3$].

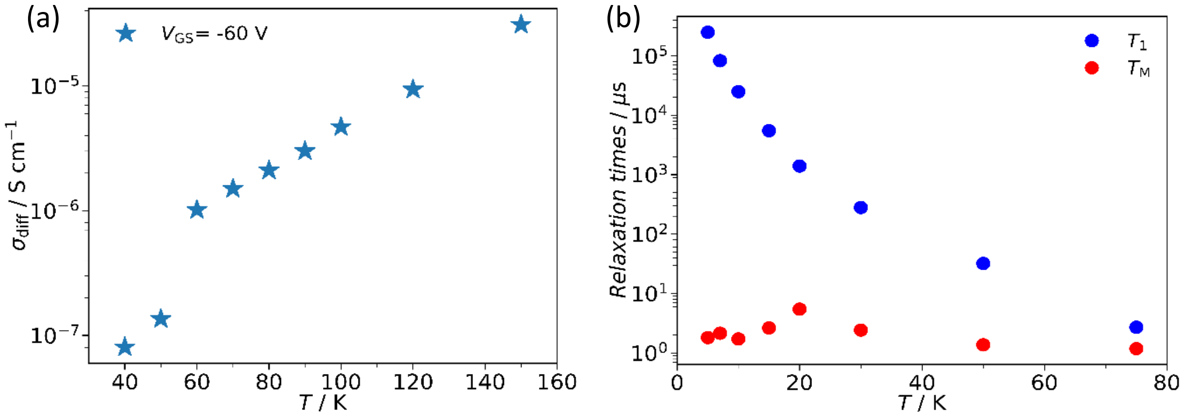

Figure 1: *(a) Differential conductivity vs. temperature for pristine PBTTT (b) spin relaxation times of [Mo(tfd-CO_2Me)$_3$]$^-$$NEt_4^+$ measured using p-EPR at 35 GHz.*

References:
[1] S. Schott, H. Sirringhaus et al., *Nat. Phys.* **2019**, 15, 814-822
[2] K. Bader, J. van Slageren et al., *Chem. Commun.* **2016**, 52, 3623-3626

In-situ CW-EPR Approach: Dihydrogen Isotopes Adsorption on A Flexible DUT-8(Ni,Co) (P-31)

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The flexible DUT-8 (Ni) is considered as a very attractive MOF due to its switchability behaviour towards external stimuli such as specific guest molecules, pressure or temperature [1,2]. Moreover, the recent literature revealed that flexible DUT-8 (Ni) selectively respond to D_2 gas while irresponsive towards HD and H_2 gas [3]. Previously, a noticeable EPR pattern for open pore phase species can be interpreted as an effective S=1/2 at the ground state level of antiferromagnetic coupling to a Co^{2+} nuclear spin in a mixed Ni^{2+}- Co^{2+} paddle wheels unit [1]. In this work, in situ CW-EPR investigation at X-band frequency has been proven as a powerful method to follow the gate opening phenomenon triggered by D_2 adsorption at 21.5 K on DUT-8(Co,Ni) materials while in case of H_2 adsorption at 19.5 K, it was no indication of pore opening.

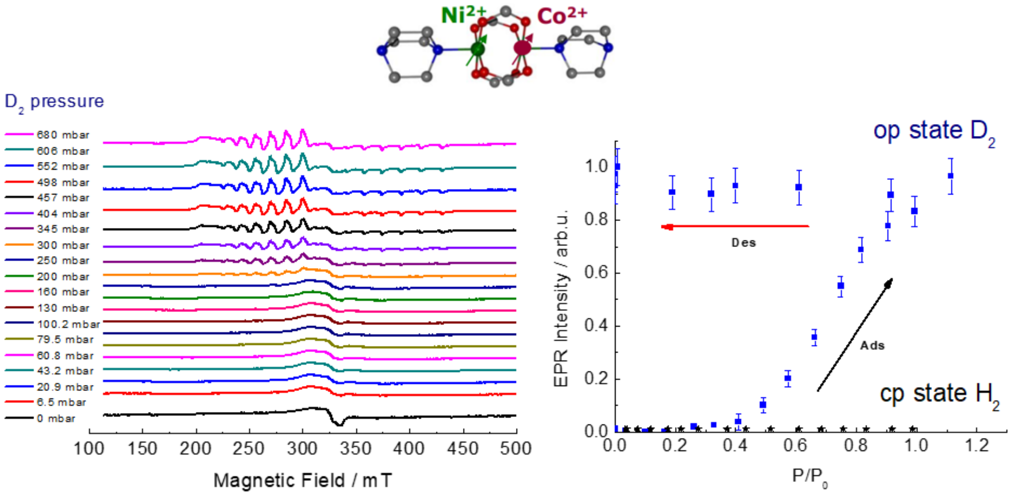

Figure 1: *Pressure dependent of D_2 adsorption recorded by in situ CW-EPR at 21.5 K (left) and EPR intensity of Co_{2+}-Ni_{2+} PW plotted as a function of the relative pressure of D_2 at 21.5 K (P_0 = 605 mbar for D_2 at 21.5 K). A structural representation of DUT-8 (Co,Ni) paddle wheel unit is given on the top.*

References:
1. Ehrling, S. et al., *Nat. Chem.*, **2021**, 13, 568–574.
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3. Bondorf, L. et al., *Sci. Adv.*, **2022**, 8, 7035.

Design of Molecular Two-Quantum Bits and Integration in Potential Quantum Devices (P-32)

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The prospect of rapid computations and high-efficiency sensing is driving the effort of researchers world-wide.[1] A variety of systems for quantum bits (qubits) are literature known and already established today. Frequently, the main focus of studies concerning qubits lies in the characterization of bulk systems like powders, crystals or solutions. The next step is the integration of qubits in devices for quantum information technologies.[2]

This work utilizes TEMPO as a well-studied, easy to functionalize molecular qubit building block which shows feasible coherence times. Two different functional two-qubit systems were synthesized employing click-chemistry. One with the goal to use as a light-switchable two-qubit system coupled to the chromophore anthracene (fig.1a), the other as precursor for immobilization in a covalent organic framework (COF) (fig.1b).

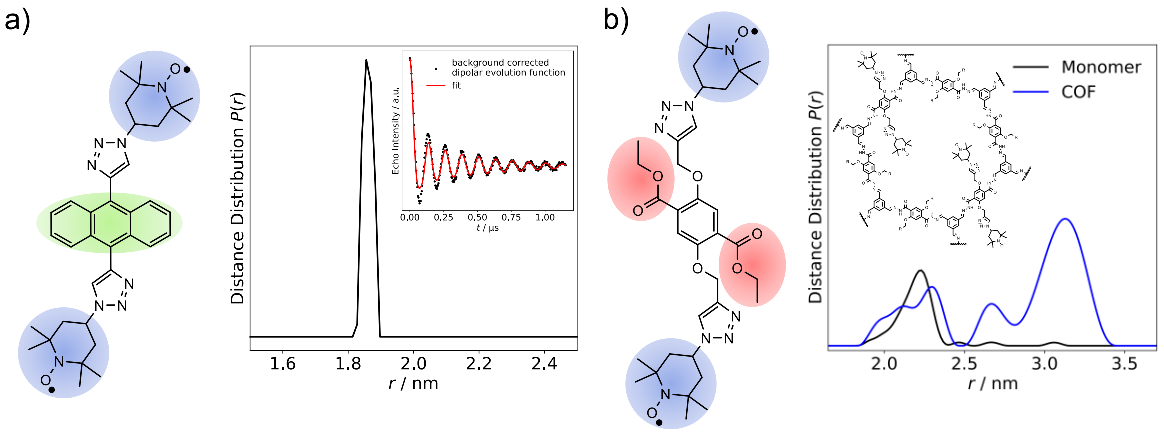

***Figure 1**: Structure of investigated compounds with corresponding DEER analysis.*

Both compounds were investigated with a variety of spectroscopic methods including pEPR and DEER. The evaluation confirmed that the coherence time T_m does not deviate considerably from the one of TEMPO (~5 µs @ 20 K), only when immobilized in a COF a decrease in T_m is observed. Additionally, individual qubit addressability was demonstrated with the help of DEER spectroscopy in all substrates, proving their potential for development in quantum devices.

References:

[1] S. A. Iyengar et al. *Adv. Mater.* **2022**, 2107839.
[2] L. Tesi et al. *Adv. Mater.* **2023**, 35, 2208998.

Pulsed Dipolar Spectroscopy Investigations of Macromolecular Multi-Spin Rotaxane Systems (P-33)

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Pulsed dipolar spectroscopy EPR techniques offer a deep insight into the nature of interactions between electron spins in close proximity [1]. Probing these spin-spin interactions enables the determination of inter-spin distances, and in some instances, the conformational flexibility of molecules via orientation selection [2]. Molecular Quantum Information Processing relies on well-defined inter-spin interactions and thus characterising these interactions is vital for identifying suitable qubit systems.

By conducting and analysing orientation-selective 4-pulse Double Electron-Electron Resonance (DEER) measurements on a series of {Cr_7Ni} [4]rotaxane systems in frozen solution, measuring the inter-ring interactions, we determine that the conformational distribution of molecular geometries adopted by the systems in solution can differ considerably from those adopted in the crystal phase (see Figure 1 for example). Structural comparison of crystal-phase and solution-phase geometries is achieved using a novel application of the Earth Mover's Distance (EMD) analysis method. Our results show that the geometric similarity between two conformation sets can be quantified by measuring the EMD between the ring coordinates or between the inter-ring metal-metal distance distributions of the two conformation sets.

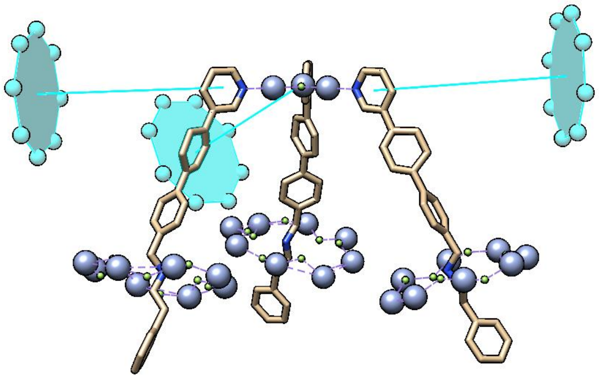

***Figure 1**: Simplified crystal structure of one of the systems studied, overlaid with the ring metal atoms in the main solution-phase conformer (cyan octagons).*

References:
[1] G. Jeschke. In *EPR Spectroscopy: Fundamentals and Methods*; D. Goldfarb, S. Stoll; Wiley: Chichester, **2018**, 401-423
[2] J. E. Lovett *et al.*, *Phys. Chem. Chem. Phys.*, **2009**, 11, 31, 6840-6848

Spectroelectrochemical EPR (SEC-EPR) for Identifying Active Sites in FeNC Catalysts (P-34)

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FeNC with FeN_4 moiety are considered prime candidates for the replacement of precious noble metals (Pt) for the oxygen reduction reactions (ORR) in fuel cells. A major problem related to FeNC catalysts is their inhomogeneity caused by the pyrolysis: beside FeN_4 units, there are iron oxide, iron carbide, elemental iron or iron nitride species present in the catalyst, some of which are accessible to electron paramagnetic resonance (EPR) spectroscopy. The presence of these species is largely influenced by its synthesis. Similarly, Iron catalysis frequently involves paramagnetic states as crucial reaction intermediates which can be identified, observed and monitored by EPR spectroscopy.
In-situ Mössbauer combined with in-situ (quasi) EPR spectroscopy is very powerful and useful in identifying iron species and determining their oxidation and spin states, especially those crucial to the catalytical mechanism. The high selectively to specific iron states such as Fe^{3+} (S=5/2) makes in-situ (quasi) EPR the ideal technique to use in combination with Mössbauer spectroscopy and shed light to the ambiguity present in Mössbauer. Alongside studies of the iron sites, in-situ (quasi) EPR detection can provide information of the nature of carbon matrix and in particular reactive oxygen species (ROS) during ORR catalysis, which until now is known little about.

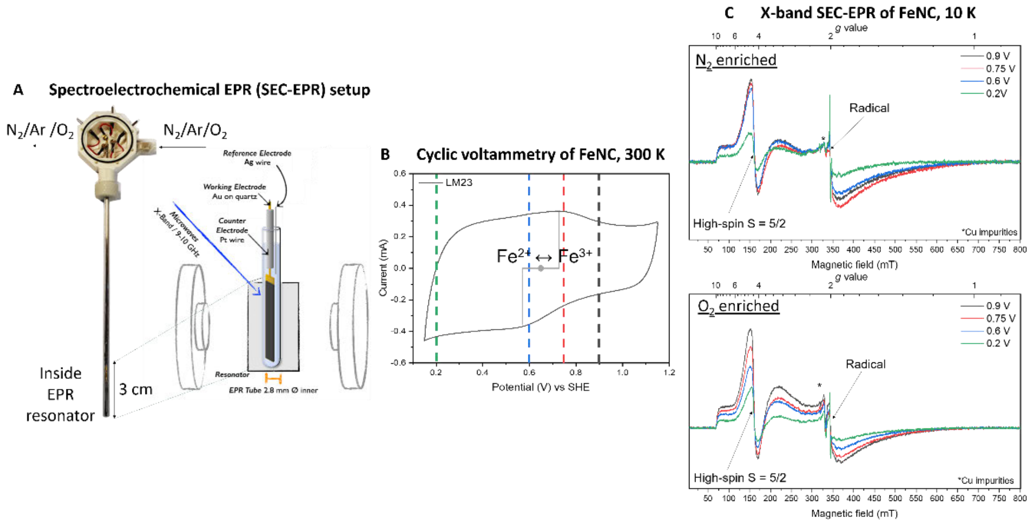

Figure 1: *(A) SEC-EPR cell, (B) Cyclic voltammogram of FeNC catalyst in SEC-EPR cell and (C) in-situ (quasi) SEC-EPR of FeNC in* N_2 *and* O_2 *environment.*

References:
[1] L. Ni, et al. Adv. Energy and Sustainability Res. 2 (**2021**), 2000064.
[2] S. A. Bonke, et al. Nat. Rev. Methods Primers 1 (**2021**), 33.

Black titania: a tricky story – A spectroscopic study on the reduction and reoxidation of titania (P-35)

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Titanium-dioxide materials are known semiconductors with many prospects in chemical catalysis, the food industry and energy conversion. Most of these applications use the photocatalytic property of titania, which is mostly active in the UV part of the electromagnetic spectrum. By chemically reducing the normally white titania, it can acquire colour, which makes it active in also the visible part of the electromagnetic spectrum. However, in literature there is a lot of contradiction on the most appropriate reduction process and its influence on the properties and photocatalytic activity of the coloured titania. In this project, titania is reduced using a thermal process with $NaBH_4$ as reducing agent [1]. It appears the reduction is sensitive to many different parameters of the process, such as the flow of argon gas through the oven. To discover which parameters actually influence the reduction, they are evaluated by systematically changing them and characterizing the reduced titania with different spectroscopic techniques, such as EPR, XRD, XPS, EELS, in-situ drift-FT-IR and UV-Vis DR. By combining the results of these techniques, it is attempted to figure out the reduction process and the importance of the reduction parameters. EPR, as one of the key techniques reveals insight in the nature of the Ti(III) centres formed upon reduction of the titania.

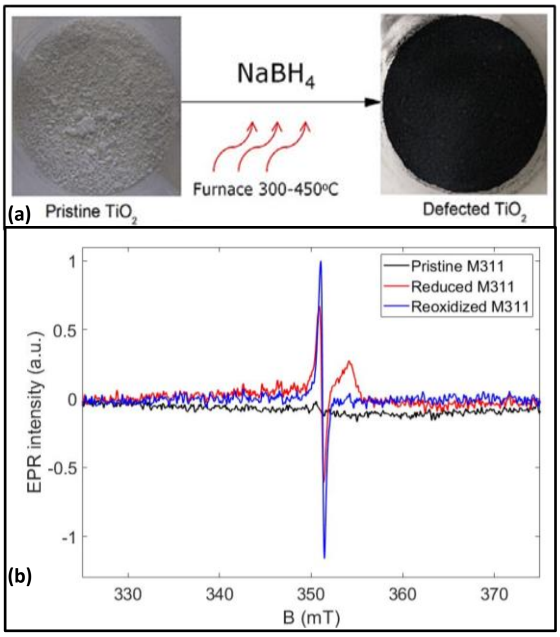

Figure 1: *(a) Reduction of titania [1]. (b) cw EPR spectra of pristine, reduced and reoxidized titania at RT.*

References:
[1] D. Ariyanti et al., *Materials Chemistry and Physics* **2017,** *199*, 571-576.

Study of Magnetic Properties of the Quantum Spin Liquid $SrCu(OH)_3Cl$ Using Electron Spin Resonance (P-36)

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We have investigated the magnetic properties of the quantum spin liquid candidate $SrCu(OH)_3Cl$ using electron spin resonance (ESR) spectroscopy at the X- band frequency (v .4 G) down to temperature T 1. K. Recently much attention has been focused on the understanding of spin S = ½ located on a triangular lattice after a perfect triangular lattice was proposed as a putative quantum spin liquid candidate [1,2]. In this context, the compound $SrCu(OH)_3Cl$ offers a unique playground [3]. It crystallizes in orthorhombic crystal structure, and this structure can be derived by breaking the planar cuprate layer to form isolated, non-planar triangular copper trimers which are connected by strontium coordination spheres. Because of the special atomic arrangement, the copper trimers form planes in which three spins form a perfect triangular structure. Importantly, each copper triangle is isolated from the others, providing an opportunity to study the magnetic ground state of isolated perfect triangular lattice.

The ESR spectra of single crystal of $SrCu(OH)_3Cl$ can be well described by a single Lorentzian line shape. The ESR intensity which is proportional to the static magnetic susceptibility can be described by a Curie-Weiss function at high temperatures. However, the inverse susceptibility deviates from the expected linear behavior at lower temperatures. The ESR linewidth shows a non-monotonic behavior as a function of temperature. It gradually decreases as the temperature is lowered, which is followed by a sharp increase at further lower temperatures. On the other hand, although the ESR g-factor increases monotonically with decreasing temperature, it changes rather rapidly at lower temperatures concomitant with the strong temperature dependence of the linewidth. Our ESR results indicate that the title compound does not exhibit long range magnetic ordering down to T = 1.8 K, but a short-range magnetic correlation begins to build up at low temperatures.

References:

[1] P. W. Anderson, Mater. Res. Bull 8, 153, (1973).

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[3] Teng-Teng Zhu et al, J. Mater. Chem. C, 2, 8170 (2014).

Revolutionizing OLED Performance: Unraveling the Role of Surface Modifiers in Enhancing Optoelectronic Performance through EPR Studies (P-37)

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Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool for studying the spin dynamics of organic and inorganic materials, and has found extensive applications in the study of organic light-emitting diodes (OLEDs). The present work investigates the capability of low-cost, and user-friendly Sodium Chloride (NaCl) as a surface modifier in OLEDs. The surface modifying characteristics of NaCl are first investigated in an OLED stack of Glass/ITO/PEDOT:PSS (hole transport layer), Super-Yellow (emissive layer), zinc oxide (ZnO) nanoparticles+PEIE (electron transport layer) and NaCl (surface modifier)/ Al, through their emission characteristics like illuminance and external quantum efficiency. Their results seem to point to an enhancement of charge transfer when adding PEIE and NaCl, leading to a better OLED performance. These findings highlight the importance of a comprehensive understanding of the spin dynamics in these OLEDs, and pave the way for the development of new and improved materials for optoelectronic applications, with low-cost and user-friendly materials.
Therefore, subsequently, EPR measurements were performed on the same OLED stacks or on simple mixtures of the different components, to better understand the role of the possible charge transfer when adding PEIE (working as injection facilitator) and NaCl (working as surface modifier), both leading to better OLED performance. Our CW EPR results demonstrate a significant charge transfer from PEIE to the ZnO nanoparticles (see figure). Moreover, time-resolved light-induced EPR reveals the dynamics and stability of this charge transfer.

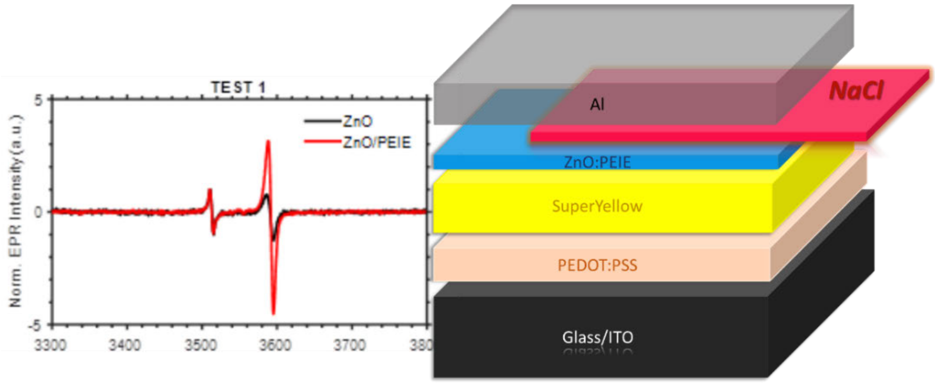

Figure 1*: OLED Stack configuration and EPR measurement of ZnO nanoparticlas alone and a blend of ZnO:PEIE*

Production and 3.5 years aging of paramagnetic point defects in ultrapure silicon irradiated with high 27 MeV electrons (P-38)

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The silicon detectors are used to monitor the position and flux of the particle beams in high-energy physics experiments at the High Luminosity – Large Hadron Collider at CERC. A better knowledge of the nature, stability and transformation properties of the radiation defects created over the operation time of silicon-based detectors helps to enhance their long-term stable performance[1]. The nature, production, transformation, thermal stability and long-term stability of the irradiation paramagnetic point defects (IPPDs) in the as-grown, n-type, phosphor-doped, standard floating zone silicon (STFZ) irradiated at room temperature with 27 MeV high energy electrons were investigated by Electron Spin Resonance (ESR)[2,3]. We investigate the nature and concentration of the IPPDs identified in the freshly irradiated and aged (stored after irradiation for 3.5 years at 250 K) STFZ samples. Anisotropic IPPDs could be observed at low temperatures (T < 120 K) in the as-irradiated and further thermal annealed samples, during "*in-situ*" illumination at 1.06 µm. Structural models based on spectra parameters and local symmetry are determined for the paramagnetic defects observed in both types of irradiated samples[4].

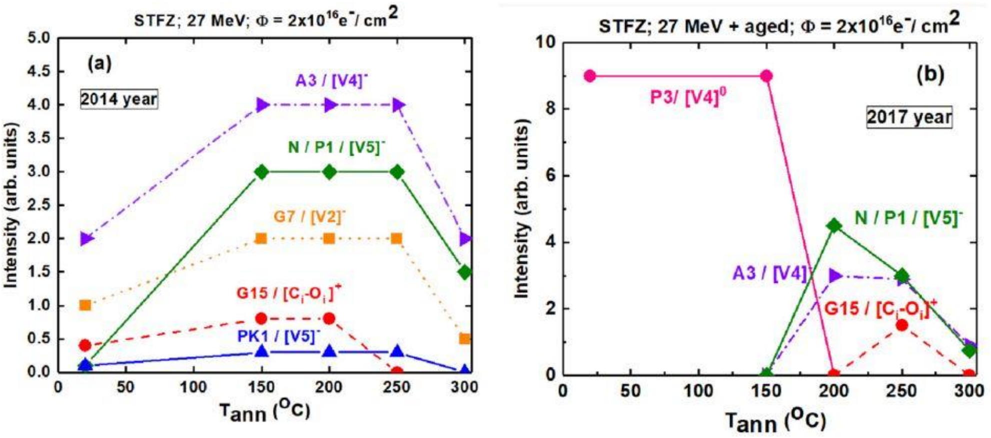

***Figure**: The relative concentration of the IPPDs identified in the ESR spectra of the STFZ samples subjected to isochronal annealing at increasing temperatures*

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Determination of site-specific kinetics in copper zeolites during Methane to Methanol conversion by *operando* EPR and UV-Vis spectroscopy (P-39)

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Methane, the main component of natural gas, has the potential as a source of fossil energy and as a raw material. Therefore, cost-effective methods to convert retained methane on-site into high-value chemicals is of great interest. So far, the industrial transformation of methane into useful chemicals and liquid fuels is only feasible via the strongly endothermic steam reforming process.

One approach, which has gained a lot of attention, is the low-temperature direct oxidation of CH_4 into CH_3OH using Cu-exchanged zeolites. [1] To improve CH_3OH selectivity, this reaction is frequently performed in a stepwise and stoichiometric chemical looping process consisting of cyclic material activation, CH_4 oxidation, and product extraction.

In this study, the Cu speciation in chabazite [2] and mordenite [3] materials exhibiting different Cu loadings and different Si/Al ratios has been studied using a combination of EPR, UV-Vis, photoluminescence, resonance Raman and FTIR spectroscopy. Apart from dimeric $[Cu2O]^{2+}$, multiple monomeric Cu^{2+} sites were found to be active. The site-specific apparent activation energies of dimeric and combined monomeric active sites were determined using *operando* EPR spectroscopy and *operando* UV-Vis spectroscopy. These findings outline the structure-performance relationship of Cu^{2+} sites in CH_4 oxidation over zeolites with different topologies.

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Spin relaxation of ferrocenium encapsulated in α-cyclodextrin (P-40)

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Single molecule magnets (SMMs) are a class of molecules able to retain their magnetization in the absence of a magnetic field [1], and have potential applications in areas such as data storage, molecular spintronic and quantum computing [2]. The SMM behavior is determined by the intrinsic magnetic anisotropy of the molecule and by the different mechanisms that allow the spin to relax and lose its coherence. The former can be qualitatively predicted by some models [3] and the latter is a hot topic in the field.

Herein, to further understand the different spin relaxation processes and how they can be affected by its surroundings we have encapsulated a molecule that we have previously studied in solid state and frozen solution, ferrocenium hexafluorophosphate, $[FeCp_2]PF_6$ [4]. We have encapsulated it in α-cyclodextrin (α-CD), Figure 1, and magnetically diluted it, and studied it by SQUID and EPR. The results show an improvement in the magnetic properties, probably due to the decrease of the dipolar interactions, isolating the SMMs, and the more rigid environment around the molecule.

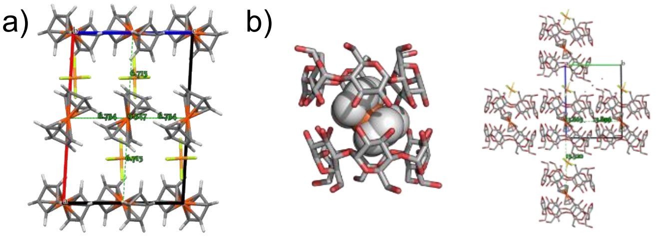

***Figure 1**:* Views of the crystal structure of (a) [FeCp]PF , and (b) encapsulated in α-C (1:)

References:

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EPR study of mixed Ni(II)/Mn(II)-*i*-MOF-74 compounds with dhia ligand (P-41)

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MOF-74, derived from 2,5-dihydroxyterephthalic acid (dhta) and various divalent transition metal nodes, represent an important class of metal-organic frameworks characterized by 1D-oxometallic nodes down the crystallographic *c*-axis, which is responsible for their unusual magnetic properties [1]. Here we present the results of the electron paramagnetic resonance (EPR) study of *i*-MOF-74 analogs based on 4,6-dihydroxyisophthalic acid (dhia), and their 1:1 intermediate complexes. Nickel(II)-*i*-MOF-74 materials (Ni-*i*-MOF-74), manganese(II)-*i*-MOF-74 (Mn-*i*-MOF-74), and their mixed analogs Ni/Mn-*i*-MOF-74 were obtained through different 1:1 M:dhia intermediates and different synthetic pathways. Despite having an identical topology as MOF-74, the different arrangement of carboxylic groups may affect the coordination sphere of the metal nodes in the chains and affect the magnetic properties of these novel materials. The goal of the work is also to understand will the different synthetic procedures influence the magnetic interaction between the metal nodes in these materials, as was the case for nascent MOF-74 [2]. Besides X-band EPR spectroscopy (Fig.1), the full magnetic characterization will be obtained by performing static magnetization measurements and multifrequency high-field high-frequency EPR (HF-EPR) spectroscopy.

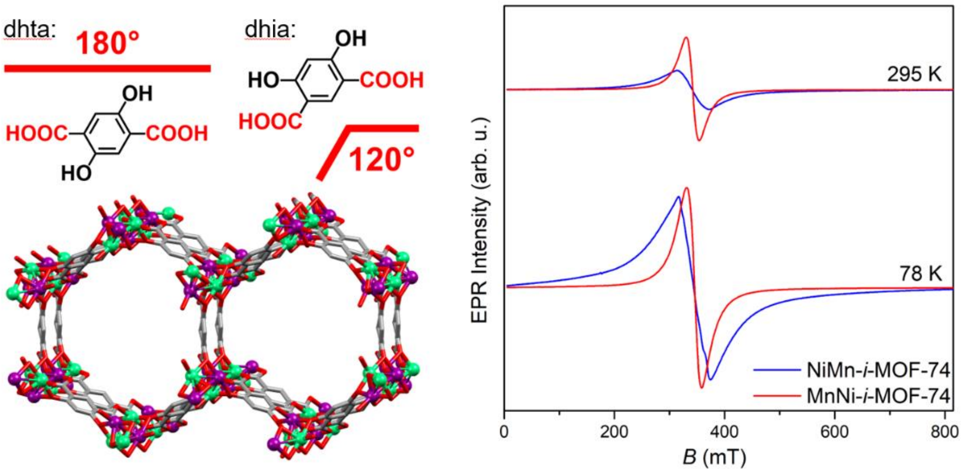

Figure 1: *Left: Structure of Ni/Mn-*i*-MOF-74 (Ni-green, Mn-violet, O-red, C-gray) with dhta and dhia structures above. Right: Temperature dependence of EPR spectra of MnNi-*i*-MOF-74 and NiMn-*i*-MOF-74 compounds.*

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Open Shell Molecular Platforms (P-42)

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The diradical behavior of open shell polymers opens many doors for emerging areas of materials research. Donor acceptor (DA) conjugated polymers (CP) can have intermediate and strong electronic correlations which allows for narrow bandgaps and diradical behavior in the ground state. In addition to the intrinsic conductivity that ground state radicals mixed with π conjugation provide the polymer systems, the diradical behavior allows for high spin states that provide emergent properties in quantum information and optoelectronics. When the bandgap becomes narrow enough, the diradical behavior forms a triplet at ground state. This high spin conformation has ferromagnetic, and electron paramagnetic resonance (EPR) has been useful in confirming that the spins are spatially localized. This high spin conformation has been found using EPR to have coherence times rivalling that of diamond NV defect qubits allowing for inexpensive and novel forms of quantum computing and sensing. The long coherence times and spatial resolution also allows for the chains to be spin addressable, aiding in quantum information efforts. This narrow bandgap is also tunable, as using different donor and acceptor monomers to traverse from an aromatic structure, to a quinoidal one, to diradicals of singlet and triplet states as described in the figure. This tunability and ability to narrow the bandgap to such an extent has allowed for novel optoelectronic materials in ranges as low energy as LWIR, areas which have recently been though of as unattainable for organic materials.

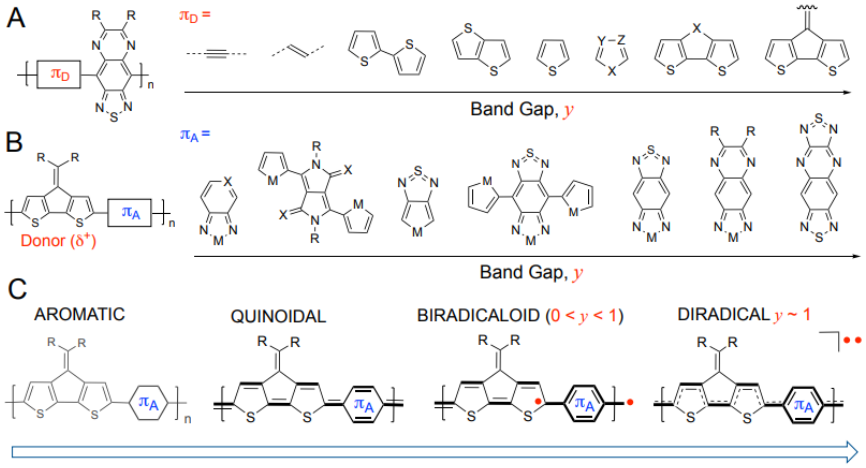

***Figure 1**: (A) Donors with solubilizing TQ acceptor and progressively narrower bandgaps. (B) Heterocyclic chemistries in combination with CPDT donor (M = S, Se; X = C, N). (C) Progression from to open-shell electronic configurations.*

High field EPR and DNP of NV Centers in Diamond (P-43)

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Dynamic Nuclear Polarization (DNP) is an efficient technique to enhance NMR signal. However, its theoretical understanding, required for fulfilling its potential, is still lacking. EPR data collected at high fields characteristic of DNP-enhanced NMR is indispensable for the analysis of DNP, due to the amount of information EPR provides about the electron spin dynamics involved in DNP. Such data is currently unavailable due to instrumental limitations, which prompted the design of our home-built high-field (14 T) DNP/EPR spectrometer.

Diamonds are good candidates for such EPR and DNP studies because of paramagnetic defects occurring in their lattice [1], which often serve as polarization agents for DNP [2]. One of the most interesting defects is the negatively charged Nitrogen-Vacancy (NV) center, as it holds unique magnetic, optical and quantum properties with long coherence times, even at room temperature [3]. These properties, make them desirable for various applications, such as sensors of minute magnetic fields, microwave amplifiers, and qubits. Here we present results of DNP and EPR experiments utilizing NV centers at high magnetic fields, which allow insights to both the V centers' electron spin dynamics and the P mechanisms, further expanding our knowledge and methodologies. This knowledge will be useful for the clarification of diamond-enhanced DNP mechanisms and for the application of NV centers in quantum technologies.

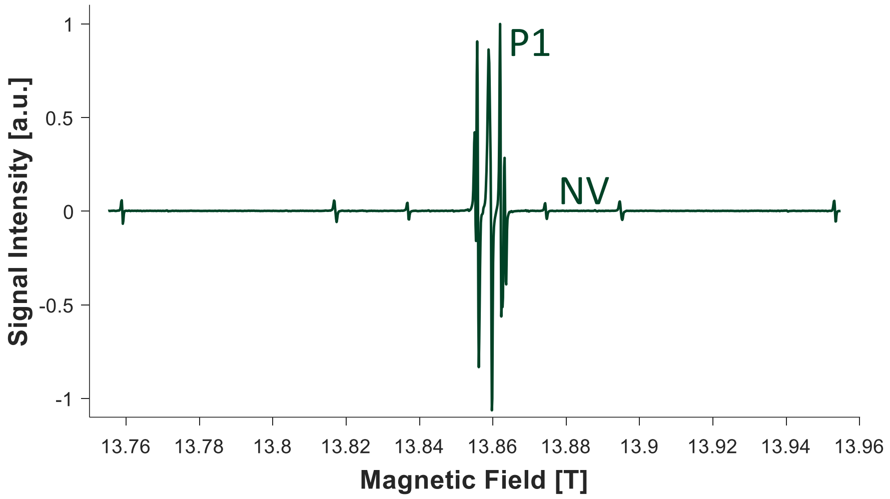

***Figure 1**: CW-EPR spectrum of diamond at 388 GHz and RT, consisting of an intense P1 spectrum and a weak NV spectrum from different orientations.*

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Operando defect characterization of high-efficiency silicon solar cells (P-44)

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In the perspective of enhancing the solar conversion efficiency of crystalline silicon solar cells above 26% (theoretical limit is ~29.3%), it is of primary importance to understand the function and reduce the influence of paramagnetic defects at the interfaces of these devices. Since their typical concentrations are below $10^9/cm^2$, they can only be characterized using electrically detected magnetic resonance (EDMR) which is orders of magnitude more sensitive than conventional EPR. In EDMR, the paramagnetic states are observed as a magnetic fingerprint in the solar cell current.
We studied 0.1 cm^2 sized solar cells which are compatible with conventional EPR resonators and still have a solar conversion efficiency of 22%. In such technologically relevant devices, we observe pulsed and cw EDMR spectra that show a hyperfine split ^{31}P signal and a resonance associated with silicon dangling bonds located either in the microcrystalline Si layer or at the interface with crystalline Si (Fig. 1b). Both signals exhibit a dramatic temperature dependence in a very small T regime (Fig. 1c). We will discuss transport and recombination mechanisms that can explain our findings and highlight possible strategies to further increase the device efficiency.

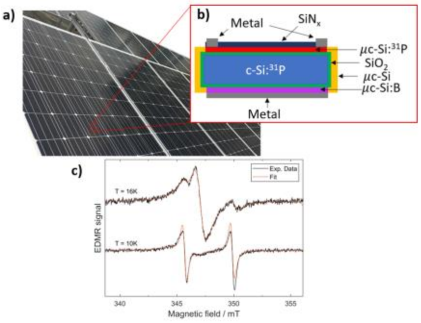

***Figure 1**: **a)** picture of solar module; **b)** schematic sideview of the solar cell; **c)** cwEDMR measurements at 10 and 16K. The spectra are a superposition of ^{31}P and silicon dangling bond signals.*

The Interface is a tuneable dimension in 3D Printed Electrodes for Oxygen Evolution Reaction (P-45)

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Water electrolysis is a process that produces hydrogen and oxygen, that then can be used as an alternative to non-renewable fossil fuels. Although it is a clean and valuable technology, it is hindered by the sluggish kinetics of the oxygen evolution reaction (OER). To address this bottleneck, researchers have explored the use of noble metal-based catalysts such as iridium and ruthenium oxides, which can improve OER kinetics. However, the high cost and scarcity of these metals limit their practical application. Numerous efforts have been made in developing metal-free catalysts and recently, carbon-based materials were found to possess unexpected performance in OER.

Carbon-based OER catalysts offer diverse structures and composition, as well as good electrical conductivity when combined with heteroatoms. In terms of electrode design, carbon's light weight and high mechanical flexibility can enhance electrode stability under higher current densities and oxygen gas evolution. Moreover, carbon's virtually unrestricted availability and low cost make it an eco-friendly and cost-effective option for large scale electrolysis technology.

This present study focuses on developing and optimizing cellulose/carbon inks for 3D printed electrodes containing metal oxides (e.g., Fe_2O_3, Fe_3O_4, Ga_2O_3, and In_2O_3) to improve the oxygen evolution reaction. 3D printing allows for precise control over the geometry and porosity of the electrode, which can enhance the surface area and facilitate mass transport of reactants and products. This, in turn, can improve the catalytic activity and stability of the carbon-based OER catalysts. To achieve these goals, the concentration-dependent rheological properties and extrudability of cellulose/carbon inks were systematically investigated to evaluate their 3D printability. Subsequent 3D printing of the optimized gel inks a variety of customizable 3D gel architectures with higher geometric accuracy and structural stability were obtained. The obtained free-standing electrodes were characterized using diverse analytical technique such as SEM, Raman, BET, and magnetic resonance techniques (solid state NMR, CW- and pulsed-EPR). The OER experiments were carried out using a three-electrode system at room temperature. Prior to each experiment, the electrochemical surface area was measured, and the turnover frequency was determined.

EPR study and molecular modelling of transition metal active centres in oxides and zeolites – applications in catalysis (P-46)

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Transition-metal-ion (TMI) exchanged zeolites and transition-metal oxides are among the most prominent catalysts in recent decades. Because of the paramagnetic nature of the active centres of both types of catalysts, EPR spectroscopy has been widely applied in studying their properties, including catalytic activity. This study aims to gain insight into the structural and electronic properties of TMI active sites and their role in selected catalytic reactions (advanced oxidation processes, AOP, and selective catalytic reduction, SCR). CW-EPR spectra of oxide-supported radicals and TMI, including copper in different environments, were analysed to obtain information about the local coordination of the catalytic sites. Furthermore, molecular modelling has been performed using DFT calculations with VASP and ORCA to substantiate the analysis. From the latter, the characteristic values of the *g* and *A* tensors have been obtained and used to assign to specific locations of the active centres and structures of paramagnetic adducts.

The catalytic activity of the materials obtained was tested in two parallel pathways: copper oxides in the aqueous phase for the generation of reactive oxygen species with applications in AOP, as well as in the gas phase in NO_x SCR using ammonia over copper exchanged zeolites. Exemplary analysis of the EPR spectra of the latter system is shown below.

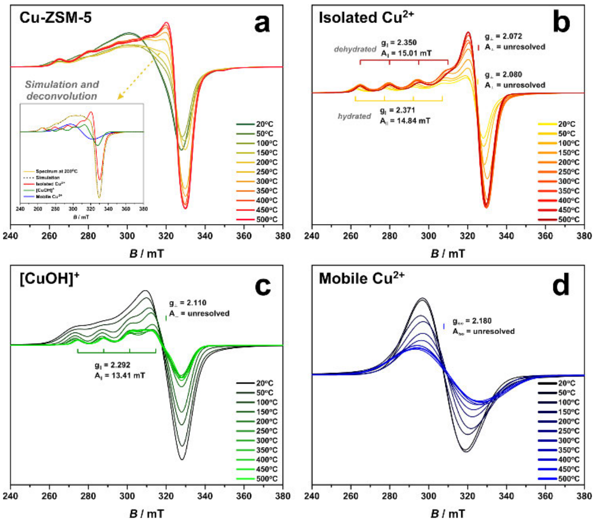

***Figure 1**: Temperature dependent evolution of copper sites in Cu-ZSM-5 zeolite*

Acknowledgements:

This work was financially supported by the National Science Centre Poland, grant Sonata Bis7 2017/26/E/ST4/00794.

Electron Spin Resonance Spectroscopy in Catalysis: Setup for In-Situ Studies and Characterization of Catalysts (P-47)

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Overcoming the ongoing climate crisis is most likely one of the biggest hurdles of the current century. It is important to decrease the emissions caused by human hand, but also to make room for additional and attractive options, for example the chemical reduction of CO_2 to useful carbon-based resources. Modern catalysis approaches, such as mimicking natures enzymatic reactions are an attractive option for succeeding in this mammoth task.[1] The use of immobilized catalysts in confined geometries could improve selectivity and catalyst stability, allowing the tailored reduction of CO_2 to C_2 and higher products, mitigating the effects of global warming.

This work is focused on novel metal porphyrins and their fused species as potential catalysts to reduce CO_2. Initial characterization of the electronic ground state by means of HF-EPR (320 GHz) and SQUID is important to understand these possible photo /electro-catalysts. Another principal tool to investigate such catalytic systems is In-situ EPR.[2] The development of this method allows to study catalysis in realistic environments, becoming more important than ever with the recent focus on first row transition metal catalysts favouring single electron transfers. The ultimate goal is to confirm the effects of confinement on catalysis by comparing the homogenous catalyst with the in mesoporous silica immobilized species.

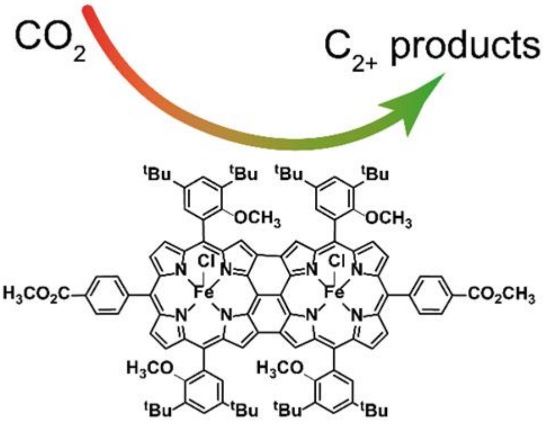

***Figure 1**: Triply fused iron porphyrin scaffold as a potential photo-/ electro-catalyst for the reduction of CO_2*

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EPR analysis of extremely coherent $C_{59}N$-C_{60} heteroazafullerene radicals entrapped in [10]CPPs (P-48)

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We have investigated organic fullerene-based spin-active molecules; $C_{59}N$ azafullerene complexes as qubits. $C_{59}N$ has an unpaired electron mainly located on the carbon atom adjacent to the nitrogen atom, therefore this radical immediately forms a stable dimer $(C_{59}N)_2$ [1].

To tackle this instability problem, our group has investigated $C_{59}N^{\bullet}$ entrapped in a [10]cycloparaphenylene ([10]CPP) ring, in which the $C_{59}N^{\bullet}$ is protected by the [10]CPP ($C_{59}N^{\bullet}\subset$[10]CPP). This complex can be generated by thermolysis of stable non-magnetic dimer [10]CPP$\supset(C_{59}N)_2\subset$[10]CPP, and we previously reported that powdered $C_{59}N^{\bullet}\subset$[10]CPP possesses a long T_1 value of 210 μs [2].

In order to improve the spin coherence time, in this study, we doped C_{60} in the system of $C_{59}N$ and [10]CPP, and carried out EPR measurements and quantum calculations. As a result, we revealed that [10]CPP$\supset C_{59}N$-$C_{60}^{\bullet}\subset$[10]CPP heterodimer with an excellent stability at room temperature was formed. The heterodimer also showed an exceptionally long T_1 about 440 μs, which is longer than any other fullerene-type radicals reported so far. DFT calculations showed that the unpaired electron shifts to the C_{60} cage in the case of the heterodimer. This novel heterodimer molecule is expected to be a long-life qubit which bridges $C_{59}N^{\bullet}\subset$[10]CPPs nearby, and further development on yield is required.

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Magnetic Resonance Spectroscopy of Thin Molecular Films (P-49)

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Molecular magnetism has been attracting the attention of scientists from diverse disciplines because of its potential applications in spintronic devices, quantum bits (qubits), and high-density information storage. Molecular magnetic compounds offer the flexibility of playing with different organic ligands around a single or multiple spins centres for obtaining a desired magnetic performance. The interplay between the magnetic and structural properties is essential for the design of new and effective materials with a specific application, such as Single-Molecule Magnets (SMM), molecules that present a slow relaxation of magnetization for data storage. High-Field Electron Paramagnetic Resonance (HFEPR) and Fourier-transformed Infrared Magnetic Spectroscopy (FIRMS) are powerful approaches to reveal magneto-structural parameters enabling the determination of the magnetic anisotropy, *g*-tensor values, and electron spin relaxation mechanisms.[1] Aiming at the potential application of these systems in devices, their ability to be deposited intact on surfaces, the characterization of the resulting thin-films and the interaction with the substrates is a necessary step. We will present recent achievements of our research group that allow the sublimation of SMM on substrates using a high vacuum chamber for the production of thin films, the characterization of bulk and thin-film materials using our home-made sample holders for HFEPR spectroscopy,[2] and a coupling mechanism of an FTIR spectrometer to our superconducting magnet allowing the measurements of FIRMS. Besides that, we will present other important techniques to evaluate the surface chemistry of the prepared thin-films, like scanning electron microscopy, X-ray photoelectron spectroscopy, and atomic force microscopy.

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2. A. Sojka *et al.* IEEE Trans. Instrum. Meas., **2022**, 71, 8002812.

EPR Analysis of Organic Radical Batteries Operation Processes (P-50)

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Redox-conductive nitroxyl-containing polymers are promising candidates for replacement of inorganic-based energy storage materials, due to their high energy density and fast redox kinetics. Organic radical batteries (ORBs) based on them can be effectively studied by EPR spectroscopy to reveal features of charging and discharging processes.

Here we report on the development of new organic cathode materials, based on TEMPO-containing Ni-Salen polymers and a versatile on-substrate electrode setup for their spectroelectrochemical EPR analysis [1]. Quantitative *in-operando* EPR experiments performed on electrochemical cells with developed polymer as active electrode material demonstrate a strong decrease in the number of paramagnetic centres upon oxidation of the film [2]. The distinct EPR signatures of the TEMPO-containing polymer and its fragments in different molecular environments are used to study the degree of electrochemical processes conversion and its degradation upon repeated cycling. A comparison between the number of EPR-active sites and the number of charges, as measured by cyclic voltammetry, provides information on the nature of the degradation process.

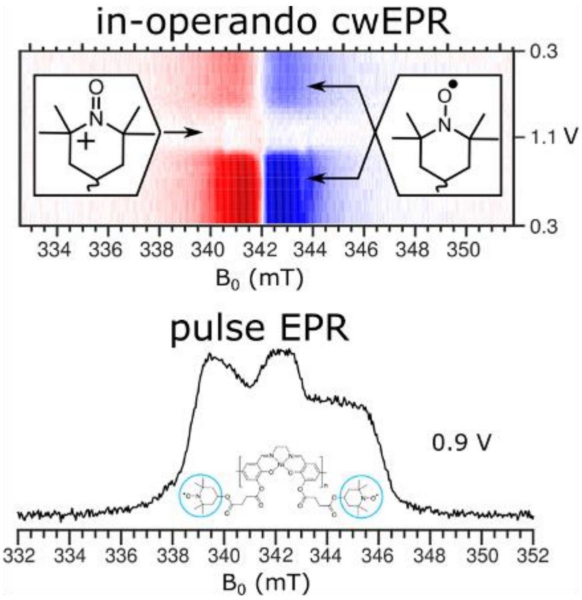

***Figure 1**: CW-EPR and Pulse EPR data*

Low-temperature ex-situ pulse EPR measurements on the oxidised polymer film reveal the spectrum of dilute nitroxide species, which indicate the formation of electrochemically inactive islands. These experiments pave the way for studying ORB materials by advanced EPR techniques.

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Temperature dependant electron nuclear double resonance (ENDOR) studies of Hydrogen Atoms in Silsesquioxane cages (P-51)

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Pulsed electron paramagnetic resonance (EPR) spectroscopy, where microwave irradiation is applied in the form of short pulses, comprises many advanced methods for the measurement of dynamic effects and the determination of weak hyperfine interactions between an unpaired electron and distant magnetic nuclei. In the field of spin-based quantum computing these methods are typically applied for the measurement of the electron spin coherence time of molecular magnets or encaged paramagnetic atoms, and their performance as quantum bits (qubits) can be evaluated [1]. Moreover, electron nuclear double resonance (ENDOR) spectroscopy can provide information on the local environment of the paramagnetic center (here: atomic hydrogen in silsesquioxane cages) [2] and thus is well suited for temperature dependant structural studies in systems lacking long-range order on length scales that are not easily accessible by other techniques.

References:
[1] G.Mitrikas et al., *Phys. Chem. Chem. Phys.* **2012**, *14*, 3782-3790.
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HFEPR spectroscopy for electric-field control of qubits in quantum paraelectrics (P-52)

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The application of ultrabroad band HFERP is promising technique to investigate the influence of an electric field on the electronic and magnetic properties of quantum materials. The coexistence of electric and magnetic degrees of freedom in paraelectric materials with spins make the electric-field manipulation of spins possible [1]. In this perspective, high field and high frequency EPR offer higher sensitivity, higher g-value resolution and access to larger zero-field splitting of spin energy levels in broad frequency range (85-1100GHz). The interplay between different HFERP techniques namely continuous wave and pulsed EPR measurements will allow the study of spin transitions induced by the electric field component of microwave and spin-electric field coupling in quantum paraelectric materials. Pulsed EPR measurement is more convenient at low temperature where the relaxation time is longer, however, measurement of high dielectric permittivity materials is challenging and require special treatment for microwaves field distribution in the resonator cavity. Spin dynamics was recently demonstrated by means of Rapid Scan HFEPR a new developed technique where sweep rate up to 300000 THZ/s was achieved in the range of 170-250 GHz [2-4]. Hence, making rapid scan EPR more advantageous for lesser resonator cavity experiments. In this poster we discuss the feasibility of HFEPR techniques: continuous wave HFEPR, pulsed HFERP and multi-frequency rapid scan HFEPR for high dielectric permittivity materials under electric field, their characteristics, limitations, and challenges will be presented as well.

References:

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[3] Laguta, O. *et al.* (2022) Appl. Phys. Lett, 120(12).
[4] Laguta, O. *et al.* (2018) J. Magn. Reson., 296, pp. 138–142.

Investigation of the charge carriers generation and reactivity of carbon modified N-TiO_2. (P-53)

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Combining oxides with carbonaceous nanomaterials is a strategy that leads to systems with improved photochemical properties and the capacity to exploit visible light [1]. We prepared different visible light active TiO_2-based materials using ammonium citrate in order to introduce simultaneously both C and N modifications. The N dopes the lattice extending the optical properties to the visible light [2], while the carbon is mainly spread on the surface. Solid state EPR was used to study the charge carriers separation under irradiation and electron transfer at the gas/solid interface. Spin trapping experiments were carried out in order to investigate the reactive oxygen species (ROS) photo-generated in solution. We found that the carbon content, modulated choosing the right synthesis parameters, has an influence on the type of ROS produced during the photocatalytic reaction. This, in turn, has a role in the final application of the system: a higher carbon content is responsible for a better efficiency in the abatement of phenol in solution while a lower carbon content is preferable for NOx degradation in gas phase.

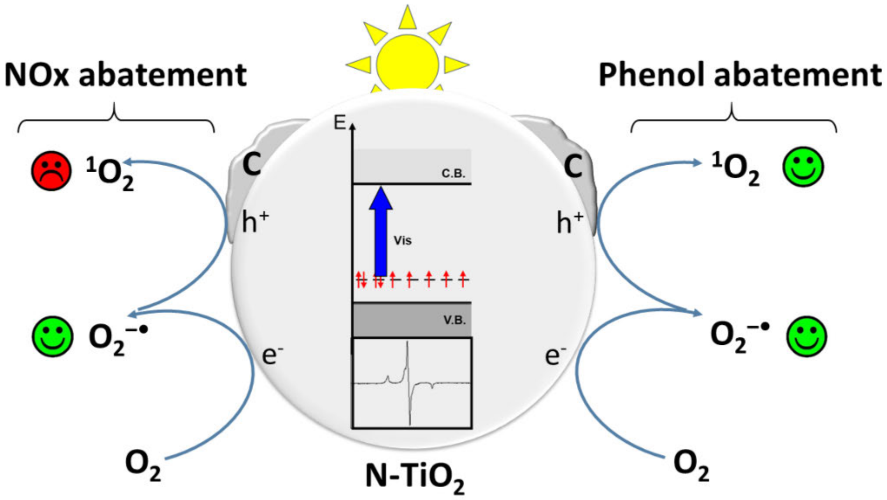

***Figure 1**: Sketch of the mechanisms operating in the two photocatalytic tests deduced on the basis of EPR evicences.*

References:
[1] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Appl. Catal. B Environ. 69 (2007) 138.
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Novel ‘molecular wires’ for long-distance electron transfer between the hierarchical electrode surfaces and redox-active molecules using Film Electrochemistry-EPR (P-54)

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Film Electrochemistry (FE) is a transformative technique allowing real-time study of electrochemical reactions with picomolar quantities[1]. When coupled with EPR spectroscopy, FE-EPR can provide simultaneous information on both reactivity and the nature of key paramagnetic intermediates[2]. Because 3D porous electrode structures are required to achieve sufficient sensitivity, this necessitates new strategies to achieve effective long distance electron transfer between the electrode surface and the redox centre of interest. Here, a series of conductive molecular wires of different lengths were designed and synthetized. These are composed of three parts: an anchoring group, a conductive wire, and a binding group (Figure 1). As proof of concept, ferrocene was anchored at the end of the conductive wire and characterized by cyclic voltammetry and EPR.

The covalent attachment of the ferrocene molecular wire onto indium-tin-oxide electrodes was demonstrated, and the dependence of the molecular wire length on conductivity was investigated. The results show that electron transfer is effective even over long distances (29.8 Å) in these hierarchical structures. EPR revels the presence of Fe(III) in the oxidised molecular wire. This work provides a foundation for anchoring complex proteins with buried redox centres onto hierarchical electrodes effectively, to enable combined protein film electrochemistry and EPR investigations.

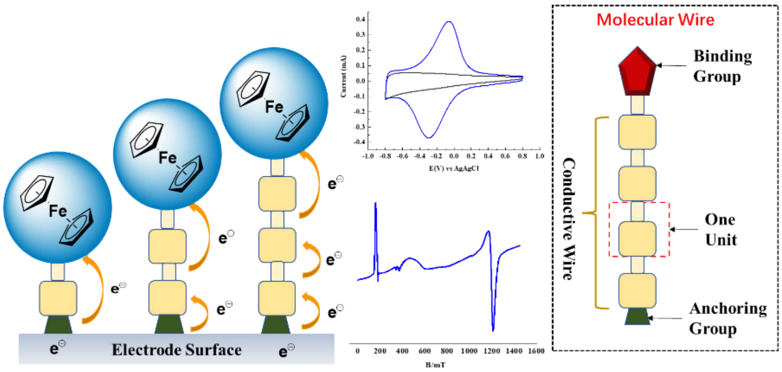

Figure 2: *the concept of molecular wire*

References:

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[2].K. Abdiaziz, E. Salvadori, K. P. Sokol, E. Reisner and M. M. Roessler, Chem Commun (Camb), 2019, 55, 8840-8843.

Simulation and experimental development of azafullerenes based qubit on diamond substrates. (P-55)

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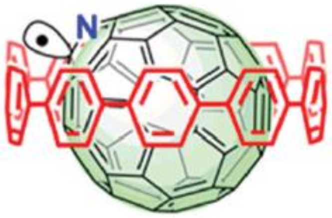
Discrete energy levels of electronic spins at the molecular level are a promising platform for realising qubits. The major challenge remains how to build complex circuits from molecular spin entities with sufficiently long coherence times. Azafullerenes ($C_{59}N$), stand out from other spin active molecules, especially when embedded in cycloparaphenylene (CPP), creating the supramolecular complex [10]CPP@$C_{59}N$, which present desired coherence times at room temperature [1], more than that its yields is better than any comparable fullerene like molecules, which is desired for scalability. The aimed quantum systems need a readout control of the quantum molecular spin states, naturally, we choose for this, the negatively charged nitrogen vacancy (NV^-) embedded in diamond substrates, already used in similar system [2].

To tackle both [10]CPP@$C_{59}N$ and NV^- we currently use density functional theory (DFT) calculation, we address the coupling between the vacancy, the separated molecules and the supramolecular complex to identify the relevant parameters of the system, surface interactions, dipolar magnetic coupling, zero field splitting (ZFS) modulation for instance. Having sufficient information, we will pursue the study by developing an experimental setup of the qubit and the readout control, through optical detected magnetic resonance (ODMR) with our NV^- centers. The goal of this work is to make a proof of concept of the system and study its scalability with related molecules [3].



$C_{59}N^{\bullet}\subset[10]CPP$

Figure 1: [10]CPP@C s upramolecular comple, showing a radical near on a carbon neighbour of the nitrogen [1].

References:
[1] Y. Tanuma et al., *Nanoscale* **2021**, 13, 19946-19955.
[2] D. Pinto et al., Nature Communications 2020, 11, 6405.
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EPR Investigation of the Electronic Structure of Multiply Oxidized Porphyrins (P-56)

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The synthesis of π-conjugated molecules with precisely tailored electronic properties is an intriguing approach towards building functional electronic materials. The distribution of single charge carriers has been extensively investigated in porphyrin nanostructures [1,2], and global aromaticity has been demonstrated in highly charged nanorings [3], but little is known about the interaction of multiple charge carriers in these systems.

In this work, we report a procedure for the chemical generation and investigation of the multiply oxidized porphyrin hexamers ***l*-P6^{N+}** and ***c*-P6^{N+}** (N = 1–6) (***Figure 1***). By combining multiple techniques including: continuous wave EPR, pulse dipolar spectroscopy, transient nutation experiments, NMR spectroscopy, as well as supporting calculations, we aim to understand the electronic structure resulting from the interaction of multiple radical electrons in a given porphyrin nanostructure. Comparisons between the linear and cyclic porphyrin hexamers in the same oxidation state will shed light on the importance of end-group effects on observed electronic structures and spin states. These results are expected to inform the design of functional molecules with well-defined electronic interactions for applications in molecular spintronics and quantum information science.

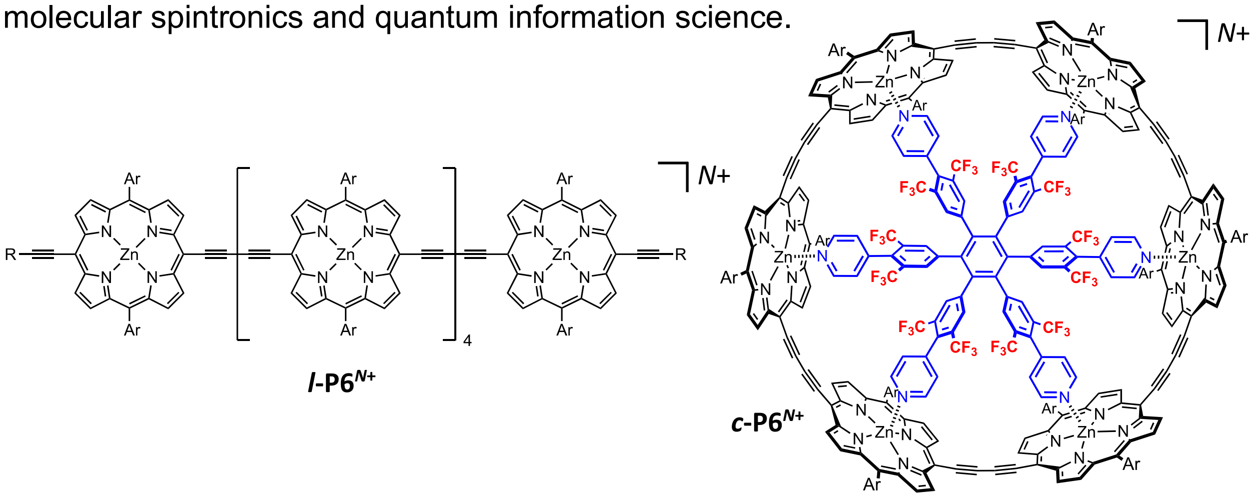

***Figure 3**: Chemical structure of the linear and cyclic oxidized porphyrin hexamers **l-P6^{N+}** and **c-P6^{N+}** (N = 1–6).*

References:
[1] M. D. Peeks *et al.*, *J. Am. Chem. Soc.*, **2017**, *139*, 10461-10471
[2] G. Moise *et al.*, *J. Phys. Chem. Lett.*, **2019**, *10*, 5708-5712
[3] M. D. Peeks *et al.*, *Nature*, **2017**, *541*, 200-202

Framework effect on the methyl group tunneling in the hybrid formate perovskites (P-57)

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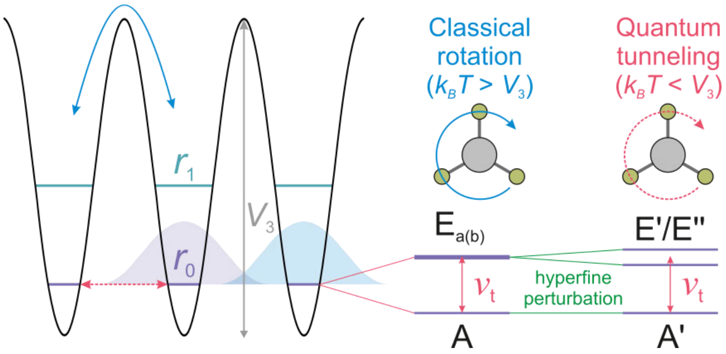
At low temperature, methyl group behaves as a quantum rotor, exhibiting rotational quantum tunneling. The tunneling frequency highly depends on a rotational barrier of the group making it a powerful tool to study its local environment. Recently, we employed Mn^{2+} and Co^{2+} paramagnetic centres to probe the methyl group tunneling in dimethylammonium zinc formate $[(CH_3)_2NH_2][Zn(HCOO)_3]$ (DMAZn) hybrid perovskite using electron spin echo envelope modulation (ESEEM) spectroscopy [1, 2].

Here, we infer how different formate frameworks effect the methyl group tunneling by measuring and analyzing the tunneling ESEEM in $[(CH_3)_2NH_2][Cd(HCOO)_3]$ (DMACd) doped with Co^{2+}. We obtain the rotational barrier of the methyl group, which is then compared to the zinc analogue.



This project has been funded by the Research Council of Lithuania (LMTLT) (agreement No. S-MIP-22-73).

***Figure 1**: Schematic energy level diagram of a methyl group rotor with rotational barrier* $\boldsymbol{V_3}$.

References:

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[2] G. Usevičius et al. Probing Methyl Group Tunneling in $[(CH_3)_2NH_2][Zn(HCOO)_3]$ Hybrid Perovskite Using Co^{2+} EPR. *Molecules* **2023**, 28.3, 979.

Spin–Electric Coupling in Copper-based Spin Triangles (P-58)

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Magnetoelectrics (ME), are materials that exhibit coupling between magnetic and electronic degrees of freedom. The linear ME effect is characterized by the absence of an inversion centre. It is generally accepted that spin-orbit coupling is required to achieve it, however, for spin-based quantum technologies, a ME avoiding it is appealing [1].

Exploration of ME effects can provide a rich playground for studying spin-charge coupling [2] and is also motivated by the potentiality to control magnetic materials by applying electric rather than magnetic fields [3].

The research group, with whom I work, has reported the detection of a ME effect on molecular helices using EPR spectroscopy under electric field modulation (EFM-EPR) attributed to an electric field modulation of the magnetic exchange [1]. Moreover, observations of a ME effect on single crystals of a non-frustrated Co(II) triangle [4] and a frustrated Cu(II) antiferromagnetic triangle [5] were observed. This technique allowed recording of the orientation dependence of ME effect with high sensitivity.

I am currently at my first PhD year doing preliminary studies on novel triangular copper molecules with an anti-ferromagnetic interaction to further understand this effect at a microscopic level.

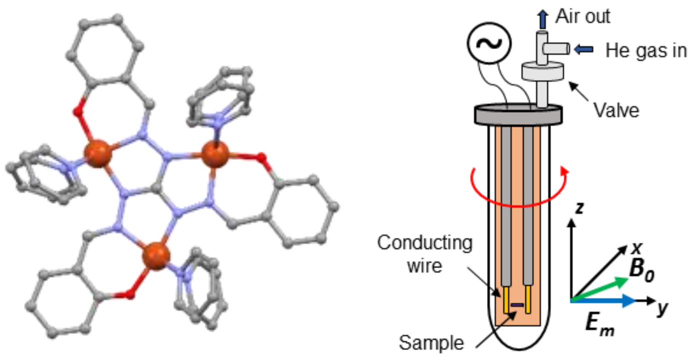

***Figure 1**: Left: molecular structure of spin-frustrated Cu_3. Right: Sample holder's schematic view.*

References:
[1] M. Fittipaldi *et al.*, *Nat. Mater.*, **2019**, 18, 329.
[2] J. Liu *et al.*, *Sci. Adv.*, **2021**, 7(10), eabf8103.
[3] N. A. Spaldin, and M. Fiebig, *Science*, **2005**, 309, 391.
[4] B. Kintzel *et al.*, *Angew. Chem. Int. Ed.*, **2021**,60, 8832–8838.
[5] Personal Communication

c.w.-EPR of Gd(III) containing chiral dinuclear cryptates (P-59)

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Lanthanide (Ln) based complexes have recently attracted much attention in the field of quantum information processing where they are proposed as quantum bits (qubits) or entanged two-qubit quantum gates [1-2]. In our group we have studied the dinuclear cryptates LnLn*L(NO3)3, with H3L = N[(CH2)2N=CH–R–CH=N–(CH2)2]3N (R = m-C6H2OH-2-Me-5) (Figure 1) [3]. These cryptates can be prepared with all LnLn* combinations with Ln,Ln*=Y, Gd-Lu. These heterodinuclear Ln cryptates can be used as model systems for two-qubit quantum gates. The two Ln ions in these complexes are also coordinated to a NO_3^- each, thus changing the symmetry of the molecule from trigonal to triclinic. This prompted us to change the cryptand so no solvent or counterion would coordinate to the Ln's. Using (S)-1,1'-binaphthalene- , '-diol (BINOL) instead of 2,6-diformyl-p-cresol, this was achieved (Figure 2). Using the chiral BINOL also makes it possible to control the chiralty of the Ln ions and synthesize resolved complexes.The difference in size of the two cryptands also means a change in the Ln-Ln distance affecting the exchange coupling between the two Ln's. The small energy scales offered by EPR gives us the opportunity to study the couplings between the two Ln's in detail. Here we focus on complexes contain Gd(III).

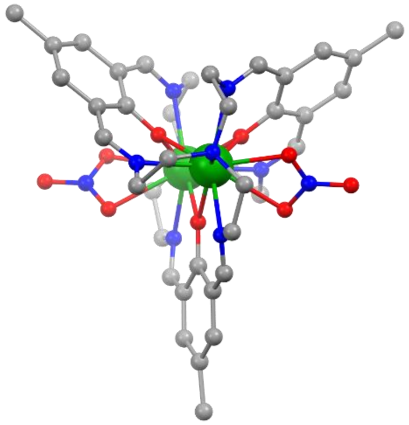

***Figure 1**: Crystal structure of $Gd_2L(NO_3)_2^+$. Hydrogens have been omitted for clarity. Colour scheme C: grey, N: blue, O: red, Gd: green*

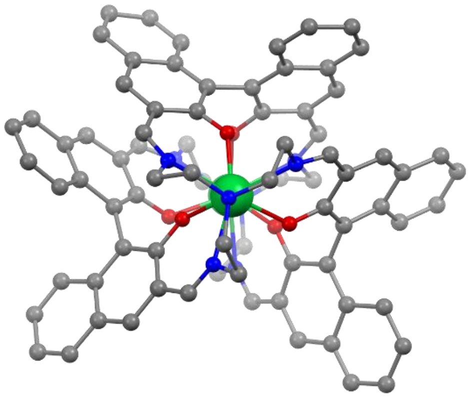

***Figure 2**: Crystal structure of $Gd_2L^{S\text{-}BINOL}$. Hydrogens have been omitted for clarity. Colour scheme C: grey, N: blue, O: red, Gd: green*

References:
[1] Aguila, D., Aromí, G. et al. (2014). J Am Chem Soc, 136, 14215-14222.
[2] Maniaki, D., Aromí, G. et al. (2022). Chem Sci, 13, 5574-5581.
[3] Buch, C. D., Piligkos, S. et al. (2021). Chem Sci, 12(20), 6983-6991.

Experimental and computational study of phase transformations and magnetism in a copper carboxylate (P-60)

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Periodic Density Functional Theory (pDFT) has been extensively used to explain and predict the structure and properties of crystalline materials, including Metal Organic Frameworks (MOFs).[1] It can predict relative thermodynamic stabilities, calculate magnetic properties, and give structural information.

We have recently shown [2] that complexes of Cu(II) and Zn(II) with 2,5-dioxido-1,4-benzenedicarboxylic acid (H_4**dobdc**) can serve as precursors for the archetypal MOF-4 [ ] family of MOFs. Importantly, the products' magnetic properties depend significantly on the metal carboxylate used in the synthesis, likely due to their differing thermodynamic stabilities. In addition, the metal carboxylates themselves, especially the copper carboxylate Cu-INT, show interesting magnetic properties.

We, therefore, decided to study these carboxylates further experimentally (PXRD, FTIR, TGA) and through pDFT. We discovered unexpected phase behavior in Cu-INT upon evacuation (Cu-INT-vac), and pDFT calculations were able to predict the existence and structure of the thermodynamically most stable form. Magnetic properties of the different phases were studied by ESR spectroscopy and magnetometry, and their thermodynamic stabilities gave new insight on the differences between the (Zn,Cu)-MOF-74 phases.

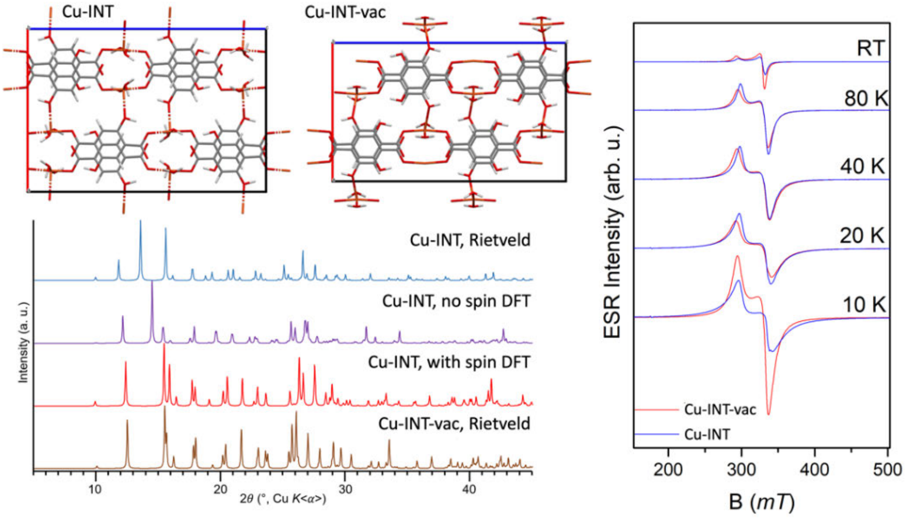

***Figure 1**: The crystal structures of Cu-INT phases. Comparison of PXRD patterns for experimental and pDFT calculated Cu-INT phases. ESR spectra of Cu-INT and Cu-INT-vac at different temperatures.*

References:

[1] D. Nazarian et al. *Chem. Mater.* **2017**, *29*, 1− .
[2] S. Muratović et al., *Inorg. Chem.* **2022**, *61*, 18181–18192.
[3] N. L. Rosi et al., *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518.

Polynuclear lanthanide compounds as molecular architectures for quantum logical operations (P-61)

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The development of physical systems for implementing quantum bits (qubits) and quantum gates (qugates) is of utmost importance for the realization of quantum computation. Electron spins embedded in magnetic molecules, such as polynuclear lanthanide (Ln) compounds, have emerged as promising candidates due to their easy manipulation and high scalability. We have designed coordination complexes with [LnLn'] or [LnLn'Ln] topology (Figure 1), which meet the requirements for two- or three-qubit quantum logical operations based on transition between the corresponding energy levels. Spin-lattice and spin-spin quantum coherence times have been assessed by means of time-dependent EPR spectroscopy, demonstrating the potential of those systems as molecular quantum gates.[1–]

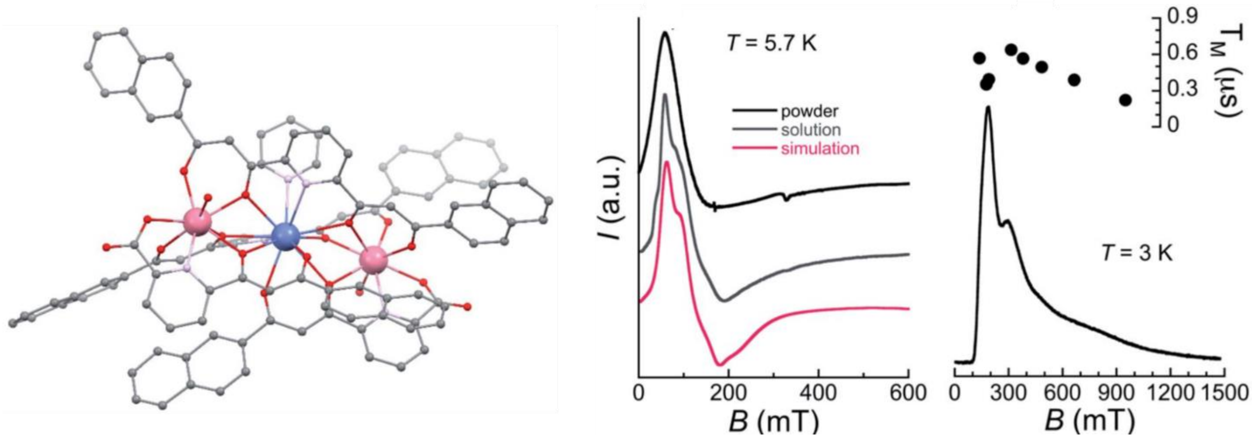

***Figure 1**: Representation of the molecular structure of [LnLn'Ln] (left) and continuous-wave (middle) and echo-detected field-swept (EDFS) X-band EPR spectra for the [ErPrEr] analogue.*

References:
[1] D. Aguilà et al., *J. Am. Chem. Soc.* **2014**, *136*, 14 1 –14
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Probing actinide covalency with pulsed EPR methods
(P-62)

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The electronic structure and the nature of bonding in *f* element compounds has been an area of interest in the last few decades. Early actinides exhibit some properties similar to transition metals mainly due to radial expansion of the 5*f* orbitals into the valence region.[1] Pulsed EPR spectroscopy methods have been previously proven as an effective tool for measuring the metal-ligand superhyperfine interaction in actinide complexes.[2]

Herein we present a study of **[U(Cp’’)$_3$]** and **[U(Cp’’)$_3$CN^{t}Bu]** U^{3+} complexes (where Cp’’ = 1,3-$C_5H_3(SiMe_3)_2^-$). We also present a first-ever study of a U^{5+} complex by pulsed EPR, **[U(BIPM)(Cp)(SPC)]** (where BIPM = bis-phosphinimino-methanide, Cp = $C_5H_5^-$, SPC = silyl-phosphino-carbene). All three complexes were studied by cw-EPR, pulsed EPR and computational methods (e.g. CASSF and HYPERION[3] calculations).

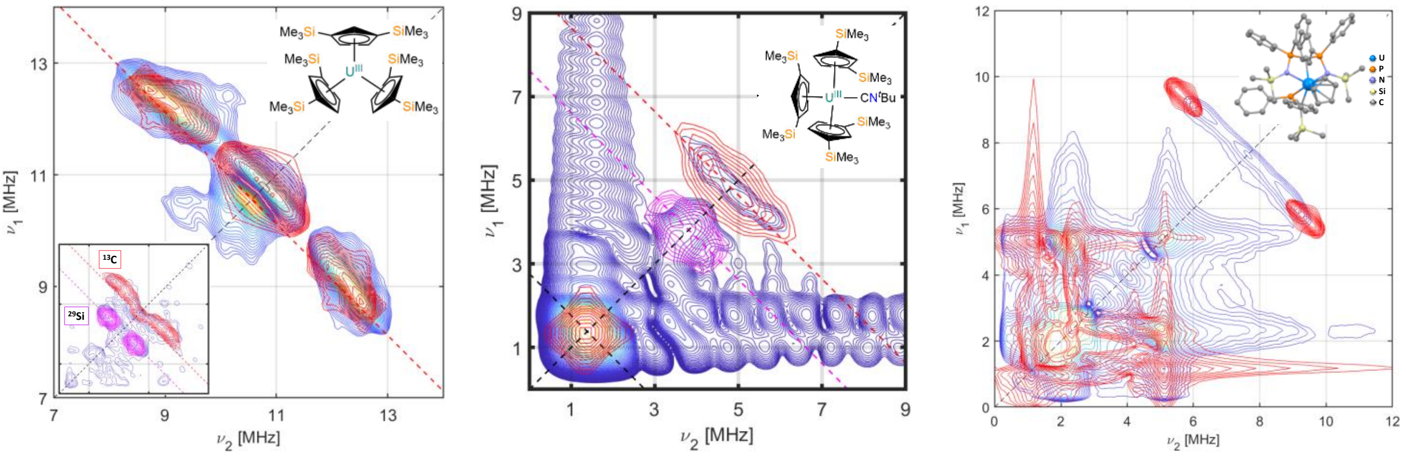

Figure 1. *X-band HYSCORE spectra of* **[U(Cp’’)$_3$]**, **[U(Cp’’)$_3$CN^{t}Bu]** *and* **[U(BIPM)(Cp)(SPC)]** *measured at 3K.*

References
[1] S. Cotton, in *Lanthanide and Actinide Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2006, pp. 145–153.
[2] Formanuik, A.-M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes and D. P. Mills, *Nat. Chem.*, 2017, **9**, 578–583.
[3] L. Birnoschi and N. F. Chilton, *J. Chem. Theory Comput.*, 2022, **18**, 4719–4732.

Principles, analytical methods and mechanisms of phototransferred thermoluminescence of calcite (P-63)

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Calcite, as do all carbonates, derives from the $(CO3)^{2-}$ anion. Calcite produces intense luminescence (TL) which is mostly attributed to presence of Mn^{2+} anions. The emission spectra of calcite [1] and carbonatite [2] consist of broadband features at lower temperatures and line structures at high temperatures. These wavelength multiplexed differences are attributed to the solubility of Mn within calcite [1]. Although there has been considerable progress in understanding mechanisms of TL in calcite, corresponding advance related to optical stimulation has been slow. In this study we combine the utility of optical stimulation with the facility of thermal stimulation to study the phototransfer (PTTL) in calcite induced by 470 nm blue-, 525 nm green- and 405 nm illumination. PTTL time-response profiles, that is, the dependence of PTTL intensity on the duration of illumination, are analysed using an eigen-value method, by use of vector fields and by theoretical modelling. We also address backscattering to donor traps and competition effects, where supposed donor electron traps suppress electron trapping at acceptor electron traps. The PTTL induced from deep electron traps by 405 nm illumination counterintuitively increases monotonically. We consider the extent to which this behaviour reflects the effect of emission over a range of excited states as predicted by the modified Orgel (1955) diagram rather than the principle 4P(4T1g). The long-term behaviour of the PTTL as studied by stability theory shows unstable critical points. The significance of this will be discussed.

References:

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EPR on biological systems

The influence of hyaluronic acid on phase transitions in pluronic systems (P-64)

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Pluronics are used as non-ionic surfactants in cosmetics, pharmaceutical formulations, in the optimization of drug delivery systems and food industry. While the regular type Pluronics form micelles, the reverse Pluronics can form different types of aggregates: flower type micelles, a micellar network or a random network. The aggregation behaviour of pluronics: F127, 10R5 and 17R4 in water and the influence of hyaluronic acid (HA), a natural polysaccharide, on the micelle formation have been investigated using EPR spectroscopy, μ SC, rheology and L S methods.

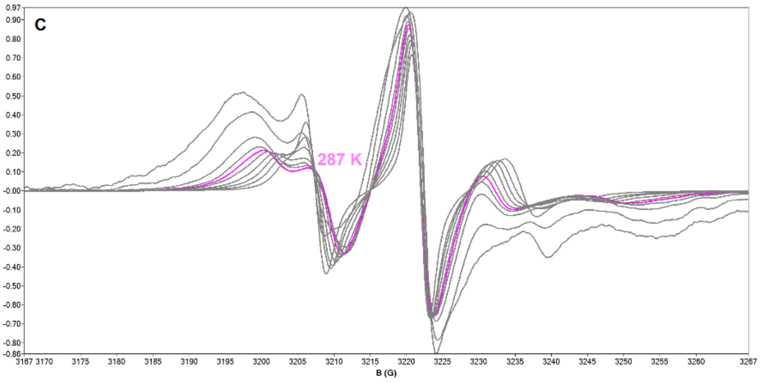

***Figure 1**: EPR spectra of 5-DSA in F127*

The 5-DSA spin probe targets the hydrophobic region in F127 and the EPR parameters show a highly restricted motion in the 273– 4 K temperature range. μ SC thermogram corresponding to F127 presents a second endothermic peak assigned to micelle-to-gel transition. HA induces a shift of the peak maximum towards a higher value.

The rheological results shown that the transition temperature from purely viscous to viscoelastic solid-like gel increases with the addition of HA. This may occur due to the disruption of Pluronic stability and self-aggregation by addition of HA. For 10R5, DLS data indicate the presence of small aggregates with hydrodynamic radius below 10 nm. HA induces a significant increase of the aggregate size which is temperature dependent. At 290 K the hydrodynamic radius is 35 nm, while at 295 K it is only 18.6 nm.

References:
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[2] M. Micutz et al., *New Journal of Chemistry* **2014**, *38*, 2801-2812

Pursuing a 20-year-old mystery – analysis of Nar1´s cofactor capacity (P-65)

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Nar1 is a proposed iron-sulfur (Fe/S) cluster trafficking component in the eukaryotic cytosolic iron-sulfur assembly (CIA) machinery known for more than two decades. The FeFe-hydrogenase-like protein has two conserved binding sites for [4Fe4S] cofactors, one of which is predicted to be a labile Fe/S cluster binding site for cluster transfer. Despite biochemical and biophysical characterization of various homologs, its cofactor binding capacity and specific function are yet still uncertain thereby complicating conclusions on its function. After developing a new purification procedure, Nar1 has now been purified with near stoichiometric amounts of iron and sulfide, based on two FeS binding sites. Spectroscopic analyses support the binding of two [4Fe4S] clusters. Furthermore, redox titrations monitored by EPR-spectroscopy also support the presence of two [4Fe-4S] cofactors, both showing very low midpoint potentials. This suggests that a redox function of the monomeric protein with two [4Fe-4S] clusters is unlikely and supports the idea of cluster trafficking to the CIA targeting complex. Our progress now allows for the pursuit of in-depth spectroscopic analyses and functional characterization of the protein.

Gd^{3+} Binding to Glycosaminoglycans Investigated by EPR (P-66)

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Gadolinium-based contrast agents (GBCA) are commonly used to enhance the quality of magnetic resonance imaging (MRI) scans by increasing the water proton relaxivity. Since Gd^{3+} ions are highly toxic, chelates of Gd^{3+} are used as GBCAs and were generally considered as safe, stable and inert.

However, Gd deposits in patients' brains, livers and other organs have been reported after administration of GBCAs [1]. Late Gd enhancement in MRI suggests Gd accumulations especially in the extracellular matrix (ECM) of inflamed tissue [2], and even dissociation of GBCA chelates. Therefore, identifying possible Gd^{3+} binding sites in human tissue is a crucial step to improve and expand GBCA application as a diagnostic tool with high specificity to the ECM.

Promising ligands for Gd^{3+} ions are sulfated glycosaminoglycans (GAGs) [3], negatively charged polysaccharides that are abundant the ECM. Some of their properties like length and sulfation pattern are found to be altered in inflamed tissue and tumors [4].

Since Gd^{3+} is paramagnetic (with a spin of S=7/2), changes in its local environment can be observed with EPR techniques and binding properties can be derived. Here, we focus on Gd^{3+} binding to different GAGs and GAG analogues. By comparing EPR linewidths, we are able to show Gd^{3+} binding and furthermore investigate the influence of sulfation and geometry of GAG analogues and native GAGs.

References:
[1] E. Blumfield et al., *Pediatric Radiology* **2019**, 49, 448-457
[2] A. Doltra et al., *Current Cardiology Reviews* **2013**, 9, 185-190
[3] M. Taupitz et al., *Contrast Media Mol Imaging* **2013**, 8, 108-116
[4] Q. Wang et al., *Polymers* **2022**, 14, 5014-5040

Conformational Changes in CRISPR-Cas13a analysed by EPR distance measurement (P-67)

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The structures and the molecular mechanism of the class 2, type VI ribonuclease CRISPR-Cas13a have not yet been fully resolved. Both crystal- and cryo-EM structures of isolated conformations during its mechanistic route from different bacteria are known[1,2,3], but until now neither the structures of all states of one organism nor the transition between these conformations could be resolved.

By combining Site-Directed Spin Labeling (SDSL)[4] and Pulsed Electron-Electron Double Resonance Spectroscopy (PELDOR or DEER)[5], we are aiming to unravel the transition of Cas13a from *Leptotrichia buccalis* from the apo- via the pre-crRNA- and crRNA-bound states to the tertiary crRNA–target RNA-bound complex. We attached two nitroxide spin labels site specifically to Cas13a by exchanging naturally occurring cysteines and introducing new ones at the site of interest by means of site directed mutagenesis. The cysteines are then reacted with MTSSL, covalently linking the label to Cas13a via disulphide bridges. Placing the labels at different sites and measuring the distance distributions between the labels with PELDOR yields a complete picture of the conformational distribution of Cas13a.

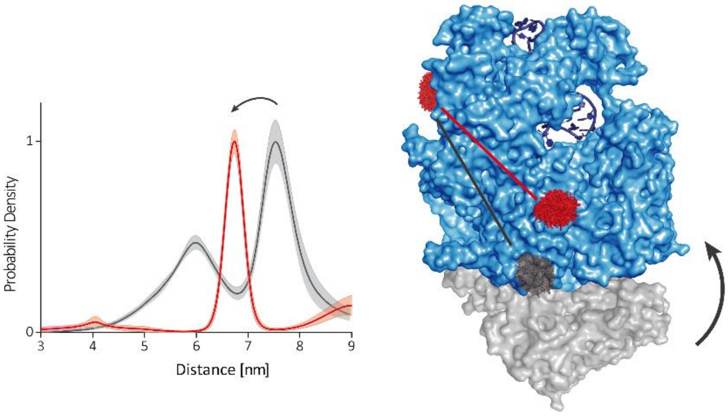

Figure 4: Left: *Apo and crRNA distance distributions of Cas13a.* ***Right:*** *A conformational shift of the crystal structure of Cas13a. The label positions and the respective distance distributions are shown in red and grey.*

References:
[1] L. Liu et al., *Cell* **2017**, 170, 714-726
[2] L. Liu et al., *Cell* **2017**, 168, 121-134
[3] G. Knott et al., *Nat. Struct. Mol. Biol.* **2017**, 24, 825-833
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[5] O. Schiemann et al., *J. Am. Chem. Soc.* **2021**, 143, 17875-17890

Design of a protein as a yardstick (P-68)

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The understanding of protein structures has great implications for health and disease, food supply and security, and biobased materials. Pulse dipolar EPR has made increasing contributions to the elucidation of structure and conformational flexibility of biomacromolecular assemblies; distance measurements in the range of up to 6 nm are well-established and applied. Examples up to 8 nm, without isotope-labelling of proteins and of up to 16 nm, with deuteration of proteins and solvent systems, have been reported but exist only for specific systems and the reports are sparse.[1,2] Hence, there exists a need for a platform where this can be systematically explored and thoroughly benchmarked.

An antiparallel homodimer is ideal for achieving a ladder rung per mutation; starting from a well-characterised 6 nm antiparallel coiled-coil,[3] we present herein a system that should allow distance measurements up to 19 nm.

Aspects of uniqueness for sequence design and charge redistribution will be shown together with structure validation through AlphaFold2, *in-silico* labelling experiments with different labels, predicted PDS data and data processing methods, to show that a 19 nm distance may indeed be within experimental reach.

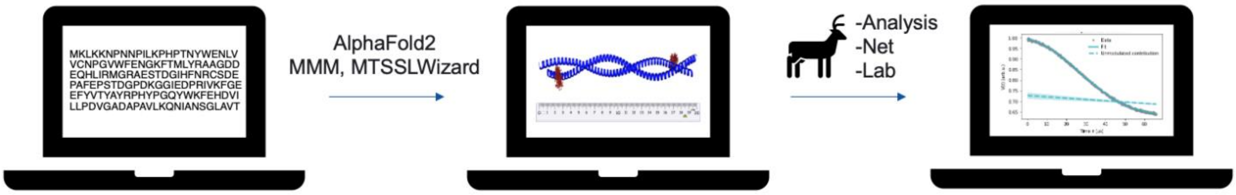

Figure 1: *Schematic workflow of the proposed in-silico validation experiment*

References:

[1] H. El Mkami et al., *Methods Enzymol.* **2015**, *564*, 125-152
[2] O. Schiemann et al., *J. Am. Chem. Soc.* **2021**, *143*, 17875-17890
[2] C. Negron et al., *J. Am. Chem. Soc.* **2014**, *136*, 16544-16556

Conformational dynamics of the major periplasmic chaperone SurA investigated using ESR spectroscopy (P-69)

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The survival protein A (SurA) plays an important role in the biogenesis of outer membrane proteins (OMPs) in Gram-negative bacteria. SurA functions as a periplasmic chaperone to aid folding and insertion of OMPs with the help of β-barrel assembly machinery (BAM) complex[1]. It has a three-domain architecture containing an N- and a C-terminal domain together forming the core domain and two peptidyl-proline isomerase domains (designated as P1 and P2). In the available structures, P2 domain is separated from the P1 domain through a flexible loop. The P1 domain closely interacts with the core domain and adopts a P1-closed or a P1-open conformation[2]. The interdomain dynamics in SurA and its relevance for function remains elusive. SurA might rapidly interchange between co-populated conformations. Since ATP is not found in the periplasm, SurA's flexible structure and conformational dynamics might serve as the foundation for its mechanism[3,4]. SurA is suggested to bind substrate in a cradle between core and P1 domains[4] or the substrate may even expand over SurA following the initial interaction[5,6]. The relative orientation of these domains or the conformational changes during unfolded OMP (uOMP) stabilization remains elusive.

We investigated the structural and dynamic basis for SurA function using pulsed ESR spectroscopy techniques. We are elucidating the interdomain interaction in SurA and conformational dynamics of both SurA and uOMP upon their interaction. Our initial results reveal a highly dynamic interdomain interaction and a coordinated movement between P1 and P2 domains.

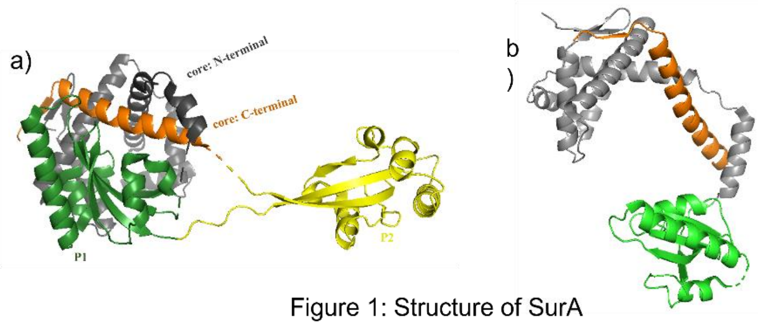

Figure 1: Structure of SurA
a) Core-P1 closed state (PDB: 1M5Y)
b) Core-P1 open state (PDB: 2PV3)

References:
[1] Konovalova *et al., Annu. Rev. Microbiol.* (2017)
[2] E. Bitto *et al., Structure* (2002)
[3] Schiffrin *et al., Commun. Biol.* (2022)
[4] Calabrese *et al., Nat. Commun.* (2020)
[5] Marx *et al., PNAS* (2020)
[6] Gao *et al.*, *Elife* 2022

EPR characterization of the heme pocket structure of nonsymbiotic hemoglobins from *Lotus japonicus* (P-70)

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Plant hemoglobins (Hbs) are found in legume nodules, actinorhizal plants and nonsymbiotic organs of monocots/dicots. Nonsymbiotic Hbs (nsHbs) have been categorized into two phylogenetic classes. Class-1 nsHbs have a high O_2 affinity and are induced by hypoxia and nitric oxide (NO) [1,2]. Class-2 nsHbs have moderate O_2 affinity and are induced by cold and cytokinins [3]. Various functions of nsHbs depend on the ability of hemes to bind diatomic ligands and catalyze the NO dioxygenase reaction.

We focus on the analysis of the ferric form of three nsHbs from *Lotus japonicus*: two class-1 nsHbs (*Lj*Glb1-1 and *Lj*Glb1-2) and one class-2 (*Lj*Glb2-1) [4]. The class-1 variants have Cys residues at specific positions in the protein chain. We focus on the difference in heme environments of the ferric wild type nsHbs and Cys variants (*Lj*Glb1-1 C78S, *Lj*Glb1-2 C79S and *Lj*Glb1-1 C8S) using CW EPR, HYSCORE, resonance Raman spectroscopy and 3D modelling of the protein structure. All forms show the heme iron predominantly in a hexacoordinated low-spin state, with proximal and distal His ligation. The difference in the EPR parameters between the variants reflects the difference in the relative orientation of the imidazole planes of the His residues. The data are compared to other plant Hbs and related to our earlier resonance Raman data of the deoxy ferrous forms of these proteins.

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[2] F. Sasakura et al., *Mol. Plant Microbe Interact.* **2006**, *19,* 441-450
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[4] B. Cuypers et al., *Front. Plant Sci.* **2017,** *8,* 407

Probing a key semiquinone intermediate in the mechanism of respiratory complex I with EPR spectroscopy (P-71)

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Respiratory complex I (R-CI) couples NADH oxidation and ubiquinone-10 reduction to proton pumping across the inner mitochondrial membrane. A semiquinone (SQ) intermediate formed during ubiquinone-10 reduction has been suggested to be key to this coupling mechanism and there have been several reports of such a g ~ 2 species observed using continuous wave (CW) EPR spectroscopy.[1] However, unambiguous assignment of observed EPR signals to a R-CI SQ has yet to be achieved.[2] Here, a synthetic membrane system and a highly sensitive EPR set-up using a cryogenic low-noise preamplifier[3] are employed to selectively investigate an organic radical species generated during R-CI catalysis (Fig. 1). CW EPR measurements reveal the presence of a piericidin A (R-CI inhibitor) sensitive radical signal at g ~ 2. To ascertain whether this signal can be attributed to a R-CI SQ, the properties, environment and location of the radical is probed using pulsed EPR techniques. Besides aiming to resolve a key step in the mechanism of R-CI, this work showcases how pulsed EPR may be used to investigate a g ~ 2 species that cannot be pinpointed using CW EPR alone.

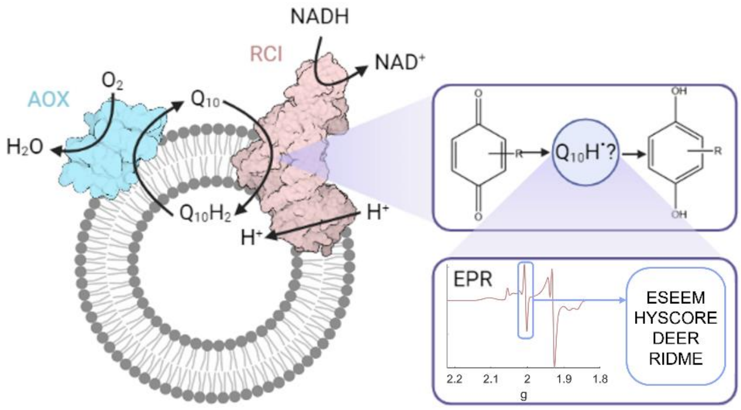

***Figure 1**: Continuous wave and pulsed EPR are used to investigate the properties and environment of a species giving rise to a g ~ 2 signal generated under sustained R-CI turnover*

References:
[1] J. Hirst, M. M. Roessler, *Biochimica et Biophysica Acta (BBA) – Bioenergetics* **2016**, 7, 872-883
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In-situ electron spin resonance spectroscopy of the β-barrel assembly machinery (BAM) complex (P-72)

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Observing membrane protein structure and dynamics in their native environments is among the major challenges for biophysicists. Pulsed electron spin resonance (ESR) spectroscopy-based techniques have emerged as a powerful tool for this purpose [1-2]. In Gram-negative pathogenic bacteria, the majority of the proteins in the outer membrane are folded and inserted by the BAM complex in the absence of an external energy source. It is a highly sought-after target for novel drugs. BAM is a penta-heterooligomeric complex and is placed in an asymmetric bilayer having a unique lipid composition. It interacts with the chaperone-substrate complex and subsequently folds and inserts the substrate into the membrane. In this project, we will address the functional mechanism of BAM using a combination of techniques including *in-situ* orthogonal labelling in the native membranes and *E. coli*, time-resolved sample preparation, and pulsed ESR spectroscopy techniques combined with structural modelling.

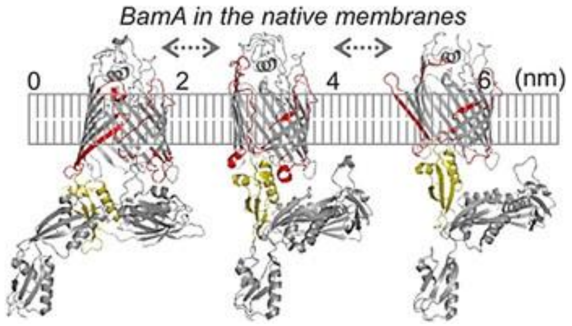

***Figure 1**: The central β-barrel BamA of the BAM complex exists in a dynamic equilibrium between different conformations in the native membranes [3].*

References:
[1] Joseph et al., *Nature Protocol* **2019**, *14*, 2344-2369
[2] Galzzo et al., *PNAS* **2020**, *117(5)*, 2441-2448
[3]. Gopinath et al., *Angewandte Chemie* **2022**, *61*, e202113448

Towards Protein NMR at Physiological Concentrations by Hyperpolarized Water and MD simulations (P-73)

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Nuclear magnetic resonance (NMR) spectroscopy is a key method for determining the structural dynamics of proteins and nucleic acids in their native solution state. However, the intrinsically low sensitivity of NMR typically necessitates non-physiologically high sample concentrations, which often limit the relevance of the recorded data. In this study, we show how to employ hyperpolarized water by dissolution dynamic nuclear polarization (dDNP) [1] to acquire protein spectra at micromolar concentrations within seconds and with a high signal-to-noise ratio.[2] The model used in our study is the transcription factor MAX (MYC-associated factor X), which we show to switch conformations when diluted. While in vitro conditions lead to a population of MAX dimer, concentrations lowered by more than two orders of magnitude entail the dimer dissociation and the formation of a globularly folded monomer. We identified this structure by integrating dDNP with computational techniques to overcome the often-encountered constraint of dDNP of limited structural information provided by the typically detected one-dimensional spectra. (***Figure 1***)

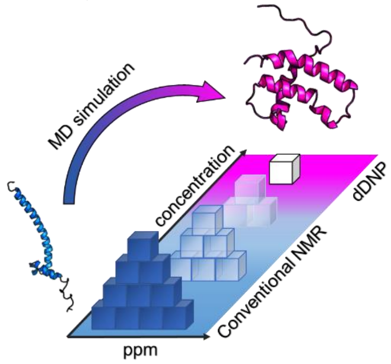

Figure 1*: The combination of dissolution DNP and MD simulations grants access to biomolecular NMR at physiologically low concentrations.*

References:
[1] C. Hilty et al., Hyperpolarized water as universal sensitivity booster in biomolecular NMR. *Nat Protoc*, **2022**. *17(7): p. 1621-1657*.
[2] Epasto, L.M., et al., Toward protein NMR at physiological concentrations by hyperpolarized water-Finding and mapping uncharted conformational spaces. Sci Adv, 2022. 8(31): p. eabq5179.

It’s about time: application of time-resolved cryo-electron microscopy and EPR to study topoisomerase dynamics

(P-74)

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The DNA topoisomerase gyrase converts the chemical energy of ATP hydrolysis into the mechanical energy of DNA torsional stress which results in the negative supercoiling of DNA required for replication and transcription in bacteria to occur. The catalytic cycle of topoisomerases involves opening/closing of protein-protein interfaces to allow passage of double-stranded DNA and large scale movements of individual domains. The intermediates with DNA in the process of transport have never been directly observed with no open interface states detected so far [1], a major challenge being how short lived the intermediates are (ms). Here, we assess the applicability of rapid spraying technique to determine high-resolution DNA-bound gyrase structures along with pulsed electron electron double resonance (PELDOR) experiments to follow movement of individual domains relative to DNA in transport.

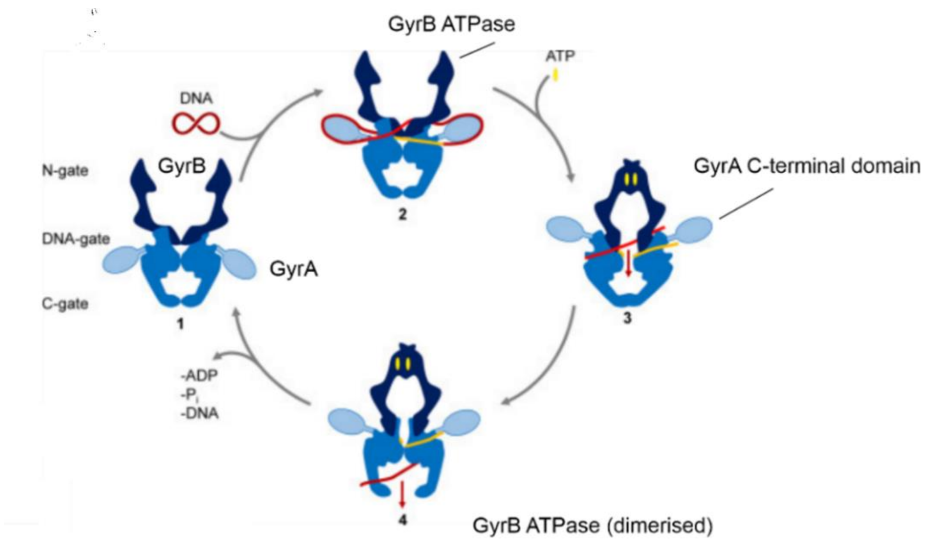

Figure 1*: DNA gyrase catalytic cycle from [2]. 3 shows trapping of the red segment in the cavity within the enzyme while the yellow segment is temporarily cleaved to allow strand passage of the red segment through the break (unobserved intermediate)*

References:
[1] A. Gubaev et al., *Nucleic Acids Res* 2016, *44*, 10354-10366
[2] Hartmann et al., *Methods in Enzymology* 2016, *581*, 317-351

EPR Spectroscopy for Investigation of Metalloproteins
(P-75)

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Metalloproteins are an essential component of every organism and play a significant role in numerous physiological processes. One-third of all proteins are estimated to require metallocofactors for their activity.[1] Electron paramagnetic resonance (EPR) spectroscopy, has been fundamental for our understanding of key metalloproteins, such as nitrogenase, hydrogenase, photosystem II, and ribonucleotide reductase. Ribonucleotide reductase (RNR), the focus of my research, catalyzes the biosynthesis of DNA building blocks in all domains of life. The active *E. coli* class Ia RNR complex houses at least five redox-active amino acid radicals (Y_{122}, Y_{356}, Y_{730}, Y_{731}, and C_{439}) that are part of the radical transfer pathway (Figure 1). Recently, our group gave insight into the in-cell structure and generation of Y_{122}• that starts the catalysis.[2] Building on this study, I investigate the in-cell generation and structure of Y_{356}•, the subsequent amino acid residue involved in the radical transfer via cw and pulsed EPR combined with site specific incorporation of unnatural amino acids.

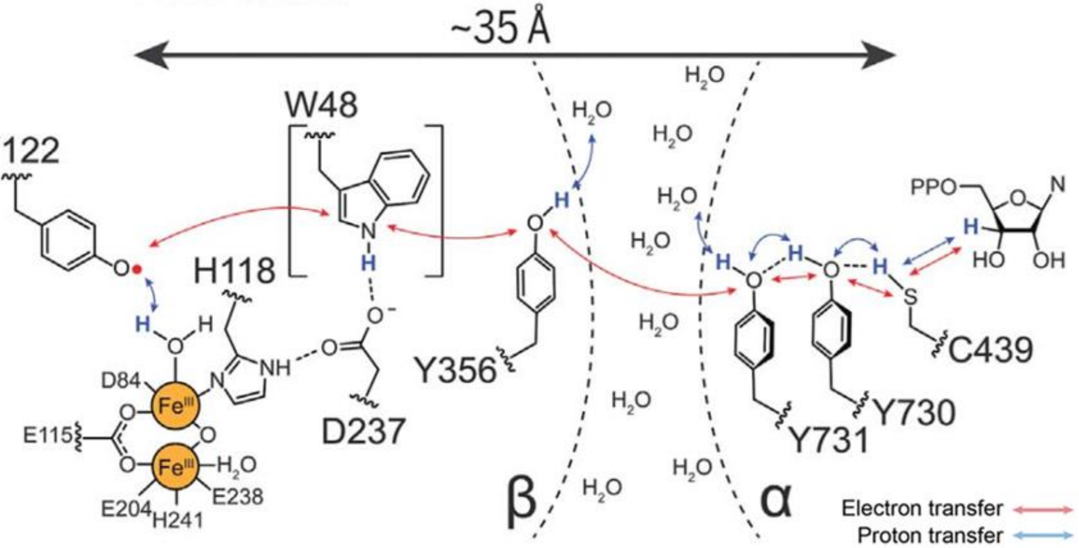

***Figure 1**: The current model of radical transfer in E.coli Ia RNR includes redox-active amino acids Y_{122}, Y_{356} in ß2, and Y_{731}, Y_{730} and C_{439} in α2.*[4]

References:
[1] J. Stubbe, D. G. Nocera, *J. Am. Chem. Soc.,* **2021,** *143,* 13463-13472.
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Using Hyperfine Spectroscopy to Map Out the Histidine-Brace in Lytic Polysaccharide Monooxygenases (P-76)

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Lytic polysaccharide monooxygenases (LPMOs) are monocopper enzymes, that catalyse the oxidative depolymerization of polysaccharides like cellulose or chitin. The active site of LPMOs is composed of the copper center, coordinated by a N-terminal histidine in bidentate fashion and an additional histidine side chain (*'Histidine Brace'*).[1] EPR Spectroscopy probes the copper center for its electronic and geometric properties, which are encoded in the **g**- and **A**-tensor. Albeit great information can be obtained from the hyperfine interaction **A**, it can often only be determined for large couplings, like $^{63/65}$Cu or ^{14}N couplings, from EPR spectra directly. To also observe smaller couplings, like ^{1}H hyperfine interactions, advanced EPR techniques, like ENDOR (Electron-Nuclear Double Resonance) can be employed.
While a variety of EPR studies for various LPMOs have been reported and discussed,[2,3] hyperfine spectroscopy has rarely been employed. Herein, we report on ENDOR experiments of the well-studied chitin active LPMO *Sm*AA10A, to determine hyperfine (and nuclear quadrupole interactions) of ^{1}H, ^{2}H, ^{14}N and ^{15}N nuclei, allowing for a detailed structural interpretation of the active site. This ENDOR study of *Sm*AA10A yields hyperfine information for each ligand, and is able to assign the various coordinating nitrogen atoms. Isotopic labelling and solvent exchanges reveal the identities of both, the exchangeable waters and amine protons.

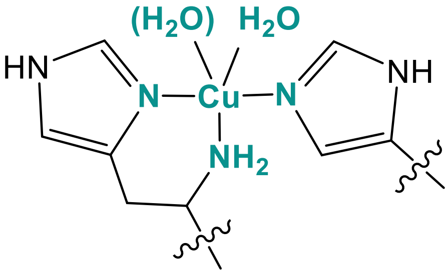

***Figure 1**: Copper Histidine Brace in LPMOs.*

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Conformations of hnRNP A1 undergoing Liquid-Liquid Phase Separation using EPR (P-77)

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EPR spectroscopy is used in this study to investigate the conformation of disordered regions in hnRNPA1, an RNA-binding protein, involved in RNA processing and localisation. The structure of hnRNPA1 consists of two tandem RNA recognition motifs (RRMs) followed by a long, flexible glycine-rich intrinsically disordered domain (IDD). The IDD has been implicated in neurodegenerative diseases such as ALS[2].

While the structure of RRMs has been solved by NMR[1], the structure of IDDs cannot be solved by conventional structural biology techniques because of its high flexibility and large conformational distribution. A further complication is that hnRNPA1 undergoes a spontaneous, concentration-dependent, reversible liquid-liquid phase separation (LLPS). The I mediates this LLPS, which may be related to this protein's involvement in ALS.

EPR spectroscopy can be used to study the structure and dynamics of disordered systems[3], such as the IDD in the liquid droplets formed in the LLPS state, once the droplets are stabilised[4].

Continuous wave EPR spectroscopy provides information on local crowding and chain flexibility at labelled residues, under different conditions. A double electron-electron resonance (DEER) experiment was used to obtain distance distributions, between two selected mutated sites[5]. These distance distributions could further be used to build ensemble protein models using RigiFlex modelling[6].

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Enabling in-cell EPR at life like concentrations and temperatures (P-78)

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The emerging field of in cell-EPR enables studying biomacromolecular structures in their natural environment by means of site directed spin labeling (SDSL) [1] and e.g. pulsed dipolar EPR (PDS) methods [2]. I will exploit reductively stable trityl radicals [3,4] to study the structure of the Yersinia outer protein O (YopO) from *Yersinia enterocolitica* [5] within different cell types. *Yersinia* bacteria cause several different diseases, the most prominent example is the plague. Since YopO is an effector protein of these bacteria [5], investigating the structure in human cells might give further insights into working mechanisms and interactions with the cellular environment during infection.

The effect of different cell types on the structure of the protein as well as on the stability of the spin label is of particular interest for this work. To optimize the transfection experiments a model system being Group G protein G, domain B1 (GB1) from *Streptococcus sp.* [6], is used. Here, I will report about first optimisation steps carried out with GB1 and following experiments with YopO to enable in cell measurements with this protein.

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Deciphering the Mechanism of DNA Cleaving DNAzyme: Insights on the Role of Manganese Cofactor Using Advanced EPR Spectroscopy (P-79)

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Deoxyribozymes (DNAzyme) are DNA molecules identified by a process known as in vitro selection [1] demonstrating their ability to catalyze chemical reaction in biological systems. DNAzyme can be designed to target and cleave specific nucleic acid sequences, operate as biosensors, or catalyze other types of reactions, such the DNAzyme of DNA [2]. Understanding the role of cofactors in DNAzyme will be crucial in developing a boosted version of DNAzyme that can compete with "amino acid-based enzymes and ribozymes" which possess a high turnover number and can even be active at stoichiometric ratios [3]. Manganese, zinc dependent DNAzyme is the core of this study. This type of DNAzyme represents a new mechanistic class for nucleic acid enzymes with a proposed radical pathway, which leads to well-defined products unlike oxidative cleavage. Both redox inactive and redox active metals coextensively support the activity of the DNAzyme. Tuning cofactors and their corresponding ratio is one of the used approaches. Hereby we capitalize on these distinctive features and by using advanced EPR spectroscopy (hyperfine, CW), we were able to detect the coupling of manganese to DNAzyme and localize the targeted region (Figure 1). We validate also the proposed radical mechanism with different approach. Our strategies and results prepare the ground for a deeper analysis as going to the utmost performance metal environment.

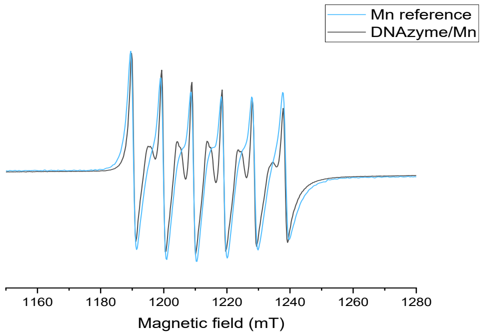

***Figure 5**: Pseudo modulated field sweeps.*

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Amyloid Aggregation by Electron Paramagnetic Resonance (P-80)

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Amyloid aggregation is a process connected to neurodegenerative diseases. In general, intrinsically disordered proteins start to fold into beta sheet aggregates called fibrils, and the oligomers formed during the aggregation are the toxic species taking part in the neurodegeneration. Characterization of oligomers is difficult with conventional techniques, due to their structural heterogeneity and transientness, which hampers the study of neurodegenerative diseases themselves. We are studying alpha Synuclein aggregation, a central process in Parkinson’s disease.

By means of site directed spin labeling (SDSL) coupled to continuous wave-electron paramagnetic resonance (CW-EPR), the aggregation process can be followed, in situ and at room temperature.

This approach allows for the study of alpha Synuclein aggregation without a separation of monomers and aggregates. The CW-EPR spectrum will thereby be composed by a superposition of components coming from labels rotating at different speeds, and simulation allows for the quantification of the amount of aggregates and of monomers in the sample.

This approach coupled to other standard fluorescent-based assays specific for amyloid fibril detection allows for the evaluation of the aggregation curves, including the toxic oligomers.

We show that in the first hours of incubation, non-fibrillary aggregates are formed and can be detected, allowing for preparation of oligomer-enriched sample and evaluation of aggregation rates.

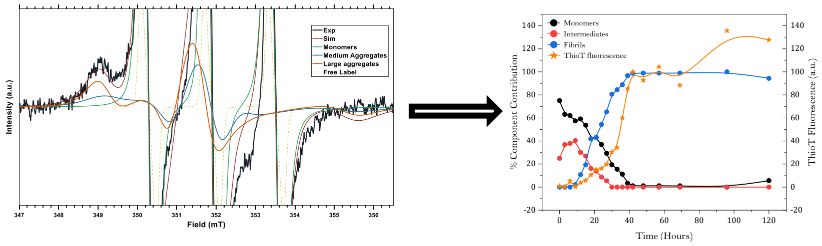

***Figure 1**: From simulation components to aggregation curves*

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Investigation of B-Box variant of HMGB1 protein interactions with heparin using EPR spectroscopy. (P-81)

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High mobility group protein B1 (HMGB1) is a highly dipolar structure: it contains of a 185-amino acid basic region, that consists of box A and box B, and a 30-amino acid cluster of acidic residues at the C-terminus. If the cell is damaged by trauma, or infection – this protein can go to the extracellular environment and act as alarmin, inducing inflammatory reaction. In some cases, this can lead to rheumatoid arthritis, Crohn's disease, sepsis, *etc.* Therefore, it is rather important to understand how it acts and how one can inhibit the inflammation caused by HMGB1. HMGB1 can bind to heparin macromolecules and this event is known to inhibit the proinflammatory activity of the protein. Heparin is a highly negatively charged polysaccharide due to numerous sulfate and carboxyl groups along the chain. Therefore, it presumably binds to the slightly positively charged parts of the HMGB1.

Here the spin labeling of the HMGB1 protein in conjunction with electron paramagnetic resonance (EPR) spectroscopy was used in order to structurally characterize the protein after its interaction with heparin. The B-Box variant of HMGB1 was successfully spin-labeled with MTSL at a position of single cysteine with thiol group. It was found out that the B-Box interacts with heparin and the maximum splitting value depends on the molar ratio of heparin to protein, suggesting that several B-Box macromolecules can bind to one heparin macromolecule depending on a heparin concentration. The unexpected change in the spectra was obtained during the interaction of the protein with unilammelar vesicles suggesting the conformational change as a spin-labeled site becomes more exposed to the solution.

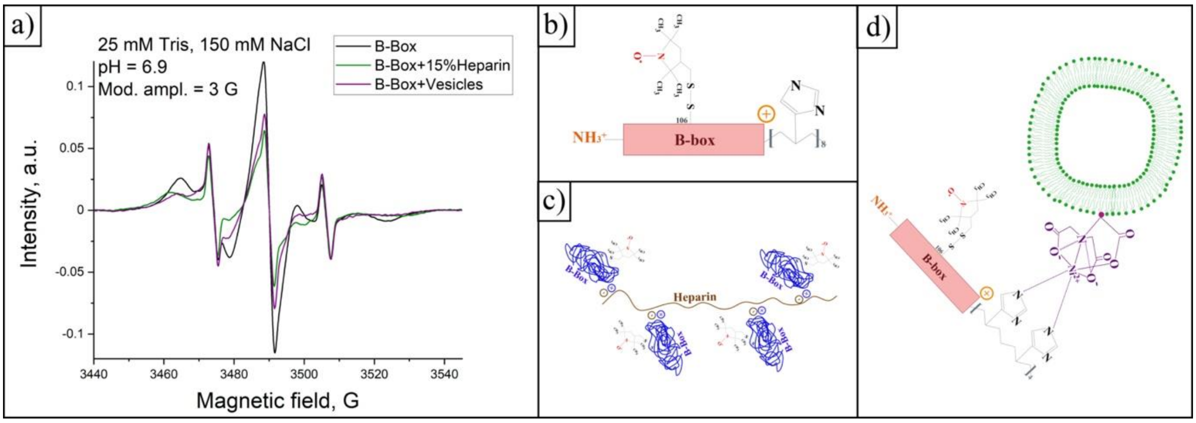

***Figure 1**: a) cw-EPR spectra of B-Box variant of HMGB1 protein spin-labeled with MTSL, with the addition of heparin ([B-Box]/[Heparin] = 0.15), and with the addition of DOPC/DGS-NTA vesicles. b, c, d) corresponding schemes.*

Electron spin resonance spectroscopy of the trans-envelope lipopolysaccharide transport system (P-82)

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The lipopolysaccharide transport (Lpt) system is a trans-envelope protein complex in Gram-negative bacteria. It mediates the transport of lipopolysaccharide molecule from the inner membrane across the periplasm into the outer membrane. In *Escherichia coli*, seven essential proteins, LptABCDEFG form the Lpt system. The inner membrane ATP-binding cassette (ABC) transporter sub-complex made of LptB$_2$FG powers the transport at the expense of ATP binding and hydrolysis [3]. It remains largely unknown how such protein complexes couple external energy into mechanical work and substrate translocation across the membrane. We aim to unravel the molecular principles underlying the energy barriers for interdomain and inter-subunit communication during long-range conformational coupling in the Lpt system. We will further develop and optimize time-resolved sample preparation and apply orthogonal spin labels for concomitant dipolar and hyperfine electron spin resonance spectroscopy experiments. Together with our collaborators we will develop appropriate kinetic models to describe the experimental data towards a comprehensive understanding of energy coupled LPS transport by the Lpt system.

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Hyperfine spectroscopy to study radical transfer in *E. Coli* ribonucleotide reductase across the α/β interface (P-83)

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E. coli ribonucleotide reductase (RNR) is a homodimeric enzyme ($\alpha_2\beta_2$) converting ribonucleotides to deoxyribonucleotides. The reaction is initiated by a long-range proton-coupled electron transfer (PCET) from β to the active site in α (Figure 1A).[1] A yet unresolved step is the PCET across the α/β interface.

^{19}F electron–nuclear double resonance (ENDOR) studies by Meyer *et al.* using 3,5-F_2Y_{731}-α_2 revealed a flipped Y_{731}-conformation with an O–O distance of ~3 Å, suggesting a colinear PCET.[2] Alternatively, water-mediated PCET has been discussed, supported by the detection of 1st coordination sphere waters in ^{17}O ENDOR studies by Hecker *et al.*.[3]

Despite the spectroscopic data provided, both hypotheses have distinct problems. While the use of fluorinated Y_{731} is a strong interference with the natural system, a water-mediated PCET requires a 2nd coordination sphere water to bridge the distance between the tyrosines (Figure 1B). Here, we present different approaches to pursue both theories. Labelling of α_2 mutants with ^{17}O tyrosine, for example, allows for detection of conformational changes via hyperfine spectroscopy with minimal perturbation of the natural system. Furthermore, we are exploring the upper distance limit of ^{17}O ENDOR with model systems (Figure 1C) to enable detection of 2nd coordination sphere water.

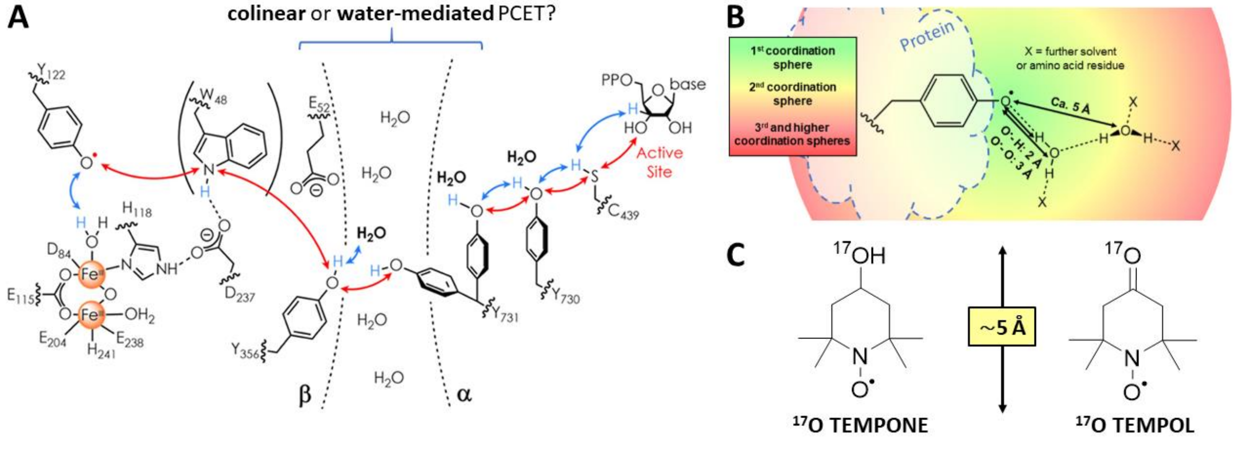

Figure 6: *A: Proposed PCET in RNR. B: Illustration of coordination spheres. C: ^{17}O model systems.*

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Electrons, Leaves and Light: Investigating the Surface Photodegradation of Agrochemicals (P-84)

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Significant population growth has caused a drive for more efficient crop production, meaning that more efficient agrochemicals are required to sustain the population. [1,2] Agrochemicals undergo photodegradation once they have been applied to the crop, [3] and an understanding of this can be exploited to develop more photostable, thus efficient, agrochemicals. In this study, novel methodologies were developed for analysis of agrochemicals and their photodegradation mechanisms on the leaf surface. The model agrochemical, Compound IV, was investigated using Electron Paramagnetic Resonance (EPR) and Liquid Chromatography-Mass Spectrometry (LC-MS) analyses. Spin trapping and scavenging techniques were used with EPR to determine whether a radical is formed on photoirradiation of Compound IV, and the kinetics of any formation that takes place. The spin trap used was 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), and the spin scavenger used was 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). A mimetic leaf surface was developed using enzyme extraction of ivy leaves to obtain the cuticular wax layer. [4] EPR analysis and optical microscopy was used to determine the suitability of this model for the investigation of radical intermediates on the leaf surface. Analytical results indicated that Compound IV photodegrades via a radical intermediate, short-lived species were formed upon irradiation of Compound IV with DMPO, and that a steady state in photo-initiated spin scavenging is reached after 20 minutes. It was also established that cuticular wax contains few intrinsic spins, making it suitable for EPR analysis. This work, therefore, laid the foundation to gain a better understanding of agrochemical photodegradation on the leaf surface.

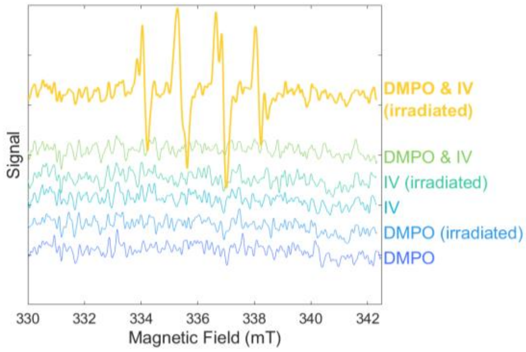

Figure 7: *Evidence that Compound IV photodegrades via a short-lived radical intermediate*

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EPR detection of mechanoradicals in aged and artificially crosslinked tendons (P-85)

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The goal of my PhD project is to obtain a more thorough understanding of covalent bond crosslinks between and within collagen molecules in tendons of specimens of advanced age, as well as tendon tissue which is subjected to oxidative stress in conditions such as mechanical trauma. In order to do so, tail and hind leg tendons collected from aged rat specimen are subjected to mechanical stress through physical pulling and stretching, and the subsequent formation of mechanoradicals is detected through cw EPR analysis [1]. The amount of mechanoradicals can be correlated with the crosslinking profile of the tendons by compared aged samples with young ones, as aging connective tissue naturally develops crosslinks in the form of AGEs (Advanced Glycation End products) which are commonly accepted to result in stiffening of the tissue [2].

In the following stage, artificial crosslinks are induced in the tendon samples through the use of crosslinking agents (Genipin, EDC-NHS, glutaraldehyde) to mimic the ageing process, and the location and amount of crosslinks are quantified to gain insight into the sites which are more susceptible to the formation of cross-chain covalent bonds. A deeper understanding of the collagen crosslinking profile could result in better treatments for age- and mechanical stress- related injuries, as well as furthering the development of artificial scaffolds and prosthetics to be used in replacement surgery.

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EPR imaging for quantifying magnetic field effects on radiation dose distributions in radiation therapy (P-86)

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In radiation therapy, accurate treatment delivery is crucial for therapeutic success. Hence, the need for methods enabling simultaneous imaging while radiation treatment leads to the rise of MR guided radiotherapy (MRgRT). This method combines irradiation by high energy (MV) photons with magnetic resonance imaging (MRI). Despite its great advantages, the strong magnetic fields (0.35 T up to 1.5 T) applied during MRgRT can cause alterations of the dose distribution. This is due to the influence of the Lorentz force on the trajectory of secondary electrons which are released in the tissue by incident MV photons. Especially the electron return effect (ERE) changes the dose distribution significantly and therefore has a clinical relevance.

However, this effect which particularly occurs on air-tissue interfaces in the body is challenging to be quantified experimentally. Höfel *et al.* recently reported on electron paramagnetic resonance imaging (EPRI) as a suitable method for the quantitative investigation of the ERE within sub-millimetre thick surface layers around millimetre-sized air cavities [1]. Based on the verification of the ERE in quartz capillaries by Höfel *et al.* (see Figure 1), the work to be presented covers the need for applying EPRI to more water-equivalent samples. By quantifying the ERE for air-cavities in Alanine pellets via EPRI and Monte Carlo simulations, more physiological conditions were examined.

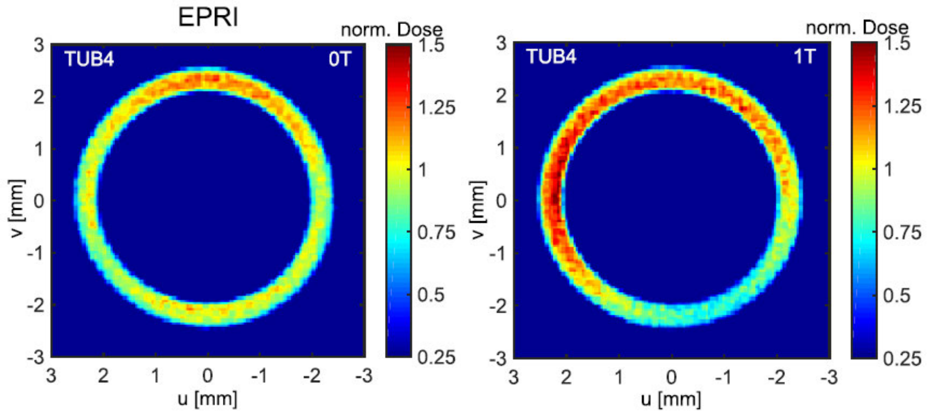

***Figure 1**: Based on EPRI experiments, reconstructed normalized dose distributions in a quartz capillary with a 4 mm air-cavity irradiated with (left) and without (right) an external magnetic field reveal the occurrence of the ERE [1].*

References:
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Revealing the reaction dynamics of NirJ and DDSH using EPR-spectroscopy (P-87)

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Cytochrome *cd*$_1$ is a nitrite reductase, which plays a key role in the global biogeochemical nitrogen cycle [1]. The active site of the enzyme contains heme *d*$_1$, a modified tetrapyrrole, as an important cofactor. One key reaction during the synthesis is catalysed by the radical SAM enzyme NirJ [2]. The substrate of the reaction is 12,18-didecarboxy-siroheme (DDSH). In this work, we find that the substrate of the reaction is present as a DDSH-NO-complex. Furthermore, we show that the substrate is bound by a tyrosine residue. Using purified NirJ/substrate complex and freeze-quench technique we can analyse the reaction dynamics of NirJ. During the reaction, we find a dynamic equilibrium of bound and unbound substrate, which leads to the assumption that the reaction of NirJ occurs sequentially.

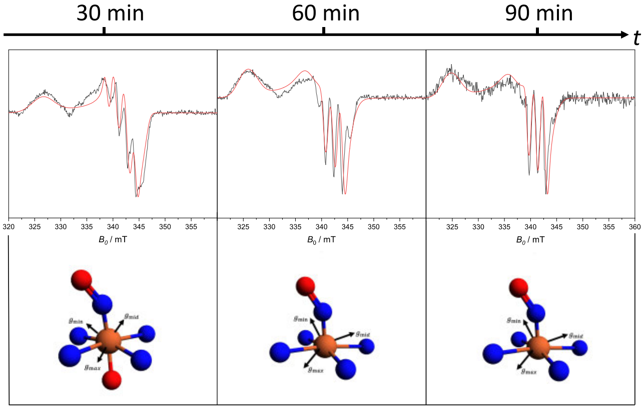

Figure 1*: X-Band cw-EPR difference spectra of NirJ/substrate complex at different reaction times. The upper panel shows the EPR spectra of the complex after certain reaction times subtracted by the spectra at t = 0. The simulation of each difference spectra is shown in red. The bottom panel shows the corresponding DDSH-NO complex of each simulation.*

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Functional and spectroscopic properties of the histidine-coordinated [2Fe-2S] cluster of the *E. coli* regulator IscR (P-88)

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Iron-sulfur clusters (Fe-S) are one of the most versatile cofactors found in nature. In the canonical clusters the iron atoms are exclusively coordinated by cysteine residues. However, the number of biological clusters coordinated by one or more non-cysteinyl ligands has been increasing rapidly[1].

Alternative ligands can be exogenous molecules or amino acids from the protein other than cysteines. Non-cysteinyl cluster coordination is found in IscR, a regulator of Fe-S cluster biogenesis (mono-histidine coordinated)[2], in Rieske proteins, involved in electron transfer[1], and in the non-Rieske oxido-reductase, Apd1, involved in cellular detoxification (both bis-histidine coordinated)[3]. The cysteine substitution by histidine is required for tuning the redox potential, coupling of the cluster's redox state with histidine (de)protonation (Proton-Coupled Electron Transfer)[1] or might be required to generate an inherent lower stability (IscR).

Electron paramagnetic resonance (EPR) spectroscopy is an excellent tool for studying Fe-S clusters as it sensitively reports on cluster type, ligands, redox state and the distance between cofactors[4]. EPR spectroscopy and mutagenesis has been applied to assess the effect of histidine coordination on the redox potential, pH dependency and stability of the IscR-bound [2Fe-2S] cluster.

As Fe-S clusters are ubiquitous in nature, their role is of paramount importance. Understanding the modulation of Fe-S clusters' properties by non-cysteine ligands is a fundamental step towards the development of new biotechnological and pharmaceutical products.

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Structural Characterization of a Mn-coordinated Enzyme from *Rhodospirillum rubrum* (P-89)

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[2]*Department of Chemistry and Biochemistry, Gonzaga University, Spokane, WA, USA*
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RquA is a bacterial enzyme involved in the biosynthesis of rhodoquinone (RQ), which is used as an electron carrier for ATP production under anoxic conditions[1]. Ubiquinone (UQ) is converted to rhodoquinone through the substitution of a methoxy group with an amino group. The amino donor for this reaction is S-adenosyl-L-methionine (SAM)[2]. While SAM is a common substrate used by radical SAM enzymes to form the 5'- deoxyadenosyl radical, the use of SAM as an amino donor is atypical. RquA requires Mn(II) as a cofactor to produce RQ[2]. In this work, both continuous wave and pulse electronic paramagnetic resonance (EPR) are used to study this Mn(II) center. X-band CW data reveals the presence of Mn(II) bound to RquA. High frequency CW EPR shows there are two distinct Mn(II) species present, both with octahedral coordination geometry. ^{14}N hyperfine sublevel correlation spectroscopy (HYSCORE) indicates the coordination of nitrogenous ligands. These results give us insight to how Mn(II) may play a role in catalysing the conversion of ubiquinone to rhodoquinone.

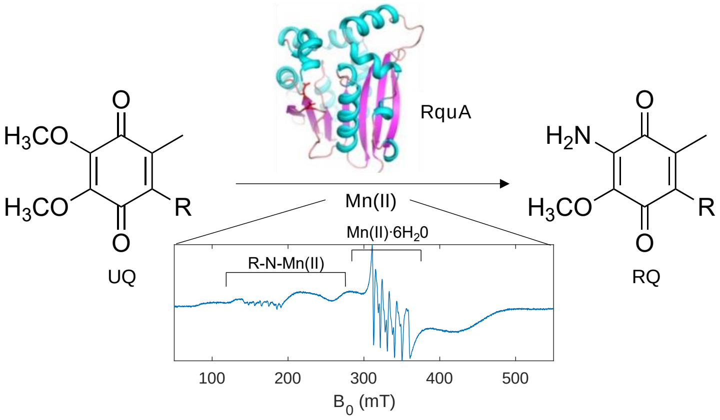

***Figure 1**: Conversion of ubiquinone (UQ) to rhodoquinone (RQ) facilitated by the enzyme RquA. Mn(II) is required to catalyse this reaction. The X-band CW EPR spectrum of in vitro RquA is shown below and indicates two distinct Mn(II) species: one indicative of hexaquomanganese, and the other indicative of a protein-bound Mn(II) species.*

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EPR spectroscopy for the study of amyloid protein misfolding (P-90)

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In recent years, protein aggregation has been associated with several neurodegenerative diseases. Electron Paramagnetic Resonance (EPR) spectroscopy in combination with spin labelling technique can be useful to investigate the aggregation kinetics of proteins in solution. However, to propose this method as a supporting complement to more conventional approaches, several studies are needed. We started studying the human alpha-synuclein, an important protein associated with Parkinson's disease. As a second unstudied protein we used a model of the amyloid-beta peptides (Aβ), associated with Alzheimer's disease, which is the salmon calcitonin (sCT). This model is useful for its low aggregation rate that allows the study of aggregation kinetics over time. Continuous wave EPR at X-band (9 GHz) was used. The spin label used was MTSSL (sulfhydryl-reactive methanethiosulfonate radical), the reactive thiol-specific spin label, which makes a disulphide bridge with the free cysteine. Regarding α-syn, to study its aggregation in vitro we performed a mutagenesis (mutation A56C). Instead in the sCT primary sequence there are two cysteine residues, which can be made accessible using DTT (dithiothreitol). An excess spin label concentration was used to maximize the binding. Measurements and simulations are in progress. The aggregation is measured as a function of time, leaving the protein at room temperature. The scope is to obtain information about the conformational changes that occur during the aggregation process. In the future we aim to test this method also on nitrobindin and human albumin for applications of EPR spectroscopy in the biomedical field.

Investigating the intermolecular interactions in PTBP1 liquid droplets by EPR (P-91)

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Liquid-liquid phase separation (LLPS) has gained much attention as the mechanism behind the formation of membrane-less organelles and its misregulation is associated with neurodegenerative diseases. PTBP1 (Polypyrimidine-tract binding protein) is an RNA binding human protein with a function in alternative splicing and other functions in post-transcription. It has been shown that upon addition of RNA, PTBP1 forms liquid droplets [1]. The goal of the project is to model the structural ensemble of PTBP1-RNA complexes in dispersed and condensed (liquid droplet) phases and to elucidate the interactions responsible for LLPS. While CW EPR spectroscopy will be used in studying short range contacts and mobility of the spin label, the key tool to modelling the structural ensemble is DEER (double electron-electron resonance). DEER allows the extraction of protein-protein, protein-RNA and RNA-RNA distance distributions, allowing a closer look at the complex net of interactions within the liquid droplets. Due to the major importance of RNA, we also want to investigate the influence of transient interactions between the intrinsically disordered inter-domain linkers of PTBP1 with RNA, which we expect to be the major driving force of LLPS in these systems. For this purpose, linear RNAs with different lengths and number of binding sites will be studied.

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EPR spectroscopy of Vanadium Nitrogenase (P-92)

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Nitrogenases are enzymes that catalyse the fixation of dinitrogen. There are three types of nitrogenases: Mo-dependent, V-dependent, and Fe-only. The catalytic moiety of nitrogenases is termed the MFe protein (M = Mo, V, or Fe) and contains two complex metalloclusters: the M-cluster, where the catalytic reduction of substrates takes place, and the [Fe_8S_7] P-cluster responsible for electron transfer. The EPR spectrum of reduced MoFe displays only a rhombic S = 3/2 signal, attributed to the FeMo-cofactor, while VFe on the same condition reveals 3 EPR signals with S = 3/2, S = 1/2 and S = 5/2. While the S = 3/2 signal on both have been attributed to the M-cluster, the S = 1/2 signal on VFe has been suggested to originate from the P-cluster. This last attribution has been sustained by studies that showed that in VFe in its apo-form (apo-VFe), i.e., without FeV-cofactor, the S = 1/2 signal persists. However, this attribution contradicts the Mössbauer [1] and crystallography [2] data on both proteins that shows that the P-cluster on both have the same structure and, in the reduced form, both should be EPR silent. With this conflicting information, the definitive origin of the S = 1/2 on VFe signal remains an open question. X-band EPR measurements in the parallel mode showed a signal at g = 11.8 associated with the two-electron oxidized state of the P-cluster (P^{2+}) in MoFe, apo-MoFe, and VFe samples, but not apo-VFe, suggesting different properties of the P-cluster in the holo- and the apo-proteins.

[1] N. Ravi *et al.*, *J. Biol. Chem.* **1994**, *269*, 20920–20924.
[2] D. Sippel, O. Einsle, *Nat. Chem. Biol.* **2017**,*13*, 956–960.

Low-spin heme centers through the lens of EPR spectroscopy (P-93)

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In the early days of biochemistry, ferric heme centers were considered a type of byproduct/waste within biological systems, since (unlike their ferrous counterpart) the Fe^{3+} form of hemoglobin loses its ability to bind molecular oxygen. It was only later that the complex roles of ferric centers in biological catalysis were uncovered. Enzymes such as catalase or cytochromes P450 rely heavily on Fe^{3+} to perform their activity, whereas others can act as sensors for small molecules owing this to the ability of ferric heme to bind a range of ligands. Understanding how such small ligands may modulate electronic and magnetic properties of heme moieties would be of great aid in material sciences and catalysis.

The present work explores the behaviour of various small strong-field ligands in their binding to ferric globins from the perspective of the temperature-dependent broadening effect and relaxation. Among these ligands, some structurally-related small moieties, upon binding to heme centers rendering specific binding cavity architecture, behave against the g strain effect. Explanations for the observed deviations are searched by DFT calculations, pinpointing how spin density distribution and hydrogen bonding network partake in magnetic properties, especially in influencing the relaxation behaviour.

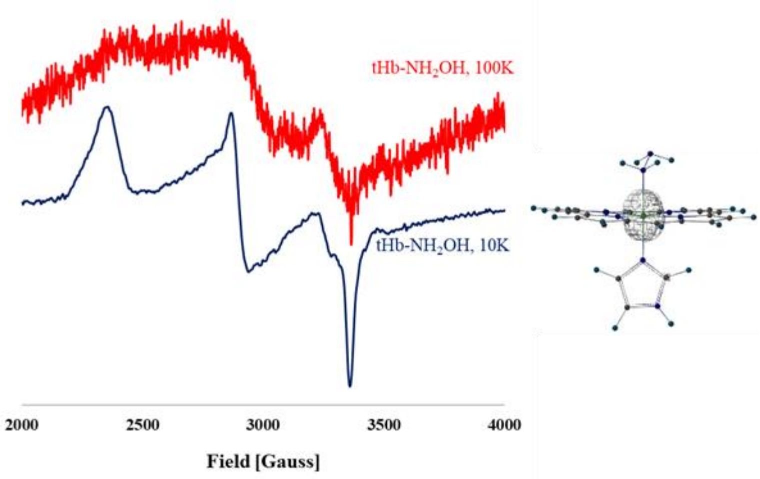

***Figure 1**: CW-EPR spectra of a truncated hemoglobin adduct with hydroxylamine (NH_2OH) at two temperatures, underlining the extent of the g strain effect. On the right is shown the corresponding spin density profile- does it matter that much? Visit my poster to find out.*

An EPR/ENDOR investigation of a Mn_2O_2 intermediate model for class Ib RNRs (P-94)

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The high valent Mn^{III}—(*μ*-oxo)$_2$—Mn^{IV} species formed in the activation of superoxide ($O_2^{\bullet-}$) in the dimanganese(II) active sites of class Ib ribonucleotide reductases (RNRs) is responsible for the formation of a stable tyrosyl radical intermediate, storing the oxidizing equivalent for subsequent enzymatic transformation.

Biomimetic approaches aim at the synthesis of dimanganese model complexes that perform such transformations. Our group recently reported the synthesis, characterization, and reactivity of a new binuclear Mn_2 complex.[1] Two different techniques, however, suggested different Mn oxidation states and O_2-binding modes in the intermediate. While resonance Raman (rRaman) shows the presence of a Mn^{II}-(*μ*-peroxo)-Mn^{III} motif (Figure 1b), its g=2 CW-EPR signal (Figure 1c, present besides a smaller g≈4 signal) exhibits the characteristic shape and hyperfine constants of Mn^{III}—(*μ*-oxo)$_2$—Mn^{IV} species, such as the $Mn^{III}Mn^{IV}$ intermediate of the enzyme co-factor.

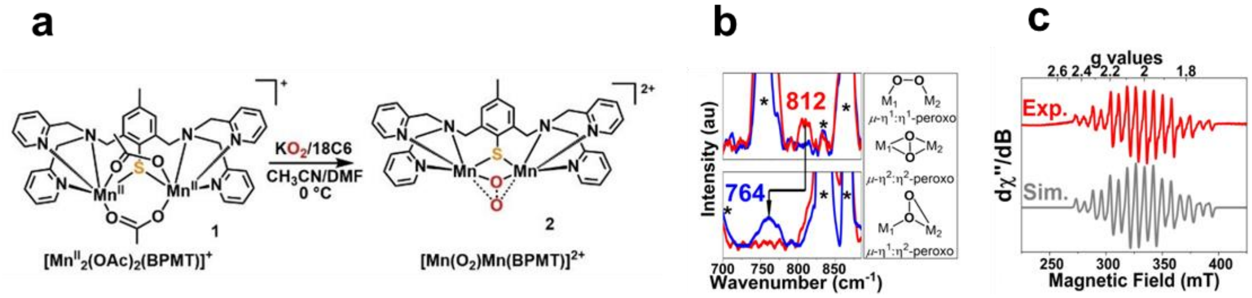

***Figure 1**: a) Reaction of $[Mn^{II}_2(OAc)_2(BPMT)](ClO_4)$ $O_2^{\bullet-}$ to form intermediate **2**. b) rRaman spectra and c) experimental and simulated CW-EPR spectra of intermediate **2**.[1]*

In this study, we aim to further investigate the binding mode for such intermediates, using different EPR techniques, such as parallel-mode and pulse EPR (Rabi nutations, ^{55}Mn Electron Nuclear DOuble Resonance (ENDOR)), focusing on understanding the Mn oxidation states associated with both the g=2 and g≈4 signals, and if there is only one or two intermediates present upon oxidation.

Our findings will contribute to a better understanding of the catalytic mechanism of class Ib RNRs and the role of key intermediates from the model for this enzyme.

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[1] B. Battistella et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202217076

EPR on photoexcited systems

Light-dependent EPR studies on radicals in carbon nitride (P-95)

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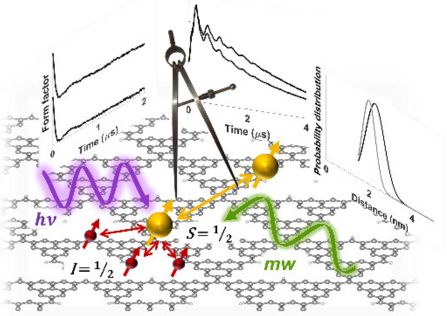
In the seek for new and more efficient catalysts to convert sunlight into chemical energy, carbon nitride (CN) is playing a crucial role thanks to its visible-light absorption, non-toxicity, available and cheap precursors and tuneable properties. Several studies suggest that either native or photoinduced radical species play a catalytic role [1]. In this perspective EPR spectroscopy offers the unique opportunity to pinpoint paramagnetic species (native radical defects, light-induced free carriers and bound excitons). We have investigated the influence of morphology and light-excitation on the number and chemical nature of radical defects [2]. Hyperfine techniques informed on the high degree of delocalisation of such species, while dipolar spectroscopy allowed to determine the spatial distribution of such defects. This latter technique, combined with the analysis of the behaviour of radicals under monochromatic irradiation, allowed to derive an energy level scheme for the intra-gap defective states. Furthermore, to reveal the nature of the chemical interaction between defects and reactants, preliminary ^{1}H ENDOR measurements have been performed on the hydrated and dehydrated CN, in the attempt to build a coordination model of an adsorbed H_2O molecule.

Another intriguing application of CN is to couple its photocatalysis with an auxiliary non-photochemical metallic centre to exploit possible synergies. I will report preliminary hyperfine data on the interaction between nickel and CN, a system used for the synthesis of high-value chemicals.



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Investigating organic solar cells using Electron Paramagnetic Resonance spectroscopy (P-96)

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Organic solar cells are considered one of the most promising solar energy technologies because of their tuneability and cost-efficiency. The active layer of these devices is composed of a blend of an electron donor and an electron acceptor. As illustrated in Figure 1, photoexcitation of the active layer generates strongly bound excitons that diffuse through the material. If they reach a donor-acceptor interface, electron transfer from the donor to the acceptor yields a charge transfer state. At this point, charges can separate into positive and negative polarons in the donor and acceptor domains, respectively, and can be extracted at the electrodes to generate electrical current.

Over the years, there has been a transition from fullerene to non-fullerene molecules used as acceptors, which has allowed a significant improvement in the power conversion efficiency, now reaching almost 20% [1]. However, the energy conversion mechanism of organic solar cells, in particular the exact mechanism of the charge separation step, is still not fully understood. Because most of the states involved, such as the charge transfer state, separated charges and triplet states, possess paramagnetic character, they can be detected and characterised by Electron Paramagnetic Resonance (EPR) spectroscopy. We aim to investigate fullerene and non-fullerene materials blended with polymer donors in both films and full devices by transient EPR and simultaneous transient EPR and Electrically Detected Magnetic Resonance (EDMR) [2]. A combined approach of these techniques was already demonstrated to be successful on fullerene materials [2] and is extended here to the characterisation of non-fullerene containing blends to highlight differences in behaviour.

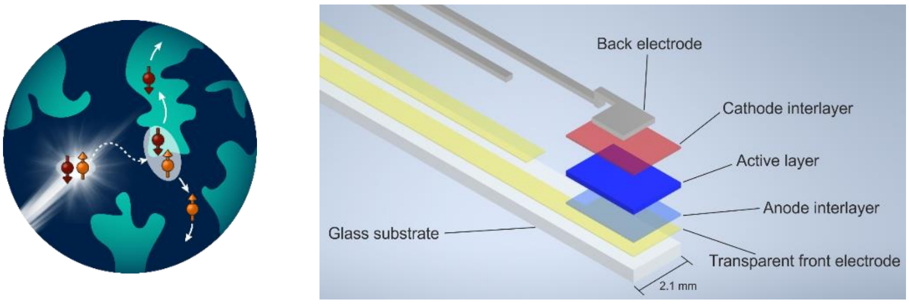

***Figure 1**: Schematic illustration of the photovoltaic process in an organic donor-acceptor blend constituting the active layer of an organic solar cell (left) and structure of a miniature organic solar cell for EPR and EDMR measurements (right)*

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[1] A. Armin et al., *Adv. Energy Mater.*, **2021**, *11*, 2003570
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Electron Spin Resonance Spectroscopy of Photoexcited Lanthanide Complexes (P-97)

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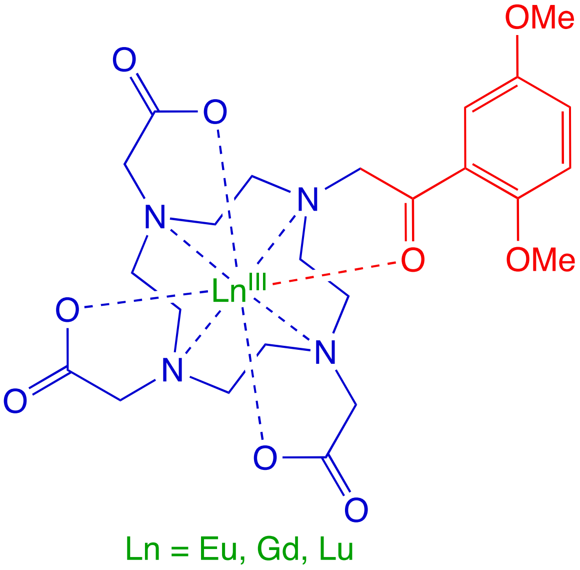
The electronic and magnetic properties of lanthanide (Ln) complexes complexes have been extensively exploited in medicine for imaging and treatment of diseases.[1] Gadolinium complexes are specifically used as MRI contrast agents due to their high spin S=7/2 ($4f^7$) ground states and slow electronic relaxation.[2] This affords T_1 relaxation enhancement for the protons in water molecules. A better understanding of the magnetic properties of lanthanide and their differing electronic states could be informative for the synthesis of improved MRI contrast agents and drug design.



Direct photoexcitation of Ln^{III} ions is often challenging due to the forbidden nature of 4f-4f transitions under electronic selection rules. By utilising a DO3A cage, a Ln^{III} ion can be directly bonded to an aryl chromophore as seen in Figure 1. Photoexcitation of the chromophore can readily afford perturbation in the electronic states of the Ln^{III} ion despite the core-like behaviour of the 4f orbitals.[3] The nature, formation and relaxation of the resulting Ln^{III} excited states can, therefore, be investigated via a variety of optical and magnetic resonance techniques.

Figure 1: A variety of different lanthanide (Ln) complexes, all featuring the 1,4-dimethoxyacetophenone-DO3A ligand. The chromophore, shown in red, is a 1,4-dimethoxyacetophenone moiety. This is bonded to a lanthanide ion, shown in green, inside a DO3A cage, shown in blue.

References:

[1] Ruijie D. Teo, John Termini, and Harry B. Gray, ***JMedChem***, 2016, **59**, 6012-6024

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Optimized Irradiation Protocol for Quantum Sensors in Hexagonal Boron Nitride (P-98)

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Color centers in solid-state materials show great potential in quantum information technology and sensing applications. The lately discovered negatively charged boron vacancy (V_B^-) in hexagonal boron nitride (hBN) [1] has shown that the defect exhibits a spin-triplet ground state with spin-dependent photoluminescence which enables for manipulation and read-out using optically detected magnetic resonance (ODMR). The system can be exploited in terms of its application as temperature, magnetic field, and pressure sensor [2,3], extending the already known applications of e.g., NV^- centers in diamond not only due to its 2D character but also by highly improved temperature sensing at low temperatures below 50K. Here we present an optimized irradiation protocol for the creation of V_B^- in hBN by nitrogen ions improving quantum metrology limits. We also present tremendous improvement of ODMR contrast showing hyperfine interaction on flakes of down to 80nm thickness.

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EPR Investigation of the Transport and Redox Conversion of Polarons in Organic Semiconductor-Based Photocatalysts (P-99)

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Heterogeneous catalysts based on organic semiconductors provide low-cost and environment-friendly solutions for energy conversion and pollution mitigation for a sustainable future, in particular if they make use of renewable and carbon-neutral energy sources such as sunlight illumination and green electricity. However, for photocatalytic proposes, effective charge separation, and thus effective utilization of the photogenerated electrons and holes, are still more difficult than in the more “traditional” metal oxide-based semiconductors. In this study, we use EPR as both a kinetic monitoring tool and a structural probe for the photogenerated polarons (i.e. electrons or holes coupled to their local chemical environment) – how they are generated, move apart and then participate in the redox reactions. The structural information from EPR *g*-values and hyperfine patterns informs us about the sites where the polarons are trapped and their kinetics. Pulsed hyperfine spectroscopy (such as HYSCORE and ENDOR), along with other methods such as transient photoluminescence and FTIR, enables us to draw more detailed information on how the catalytically active site is organized. Overall, our studies reveal that the cooperative action between structural motifs that enable light absorption and ion conduction in such photocatalysts enables more efficient generation of EPR-detectable polarons and enhances photocatalytic activity, sometimes approaching that of metal-oxide semiconductors.

In-situ EPR study of photo-Fenton-like catalysts for waste water treatment (P-100)

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Contaminants of emerging concern (CECs) are increasingly detected in surface water. Since they are highly persistent, the use of advanced oxidation processes (AOP), such as Fenton catalysis combined with sunlight, is a method of choice for sustainable wastewater treatment. To overcome the limitations of classical homogeneous Fenton catalysis, we have developed a new class of heterogeneous Fenton-like catalysts working at near-neutral pH and during visible light irradiation [1]. In these catalysts, Mn, Cu, and Fe are used as active sites in/on a mesoporous silica support. Different molar ratios of metal to Si have been used to prepare combinations of mono-, di-, and tri-metal mesoporous silica (Mn/Cu/Fe-MS) supported photocatalysts. The efficiency of the photocatalysts was tested for the degradation of bisphenol A, a model organic CEC in water. We used in-situ electron paramagnetic resonance (in-situ EPR) to monitor paramagnetic centres formed upon irradiation in solid samples [2] and paramagnetic intermediates formed during the photocatalytic reaction by spin-trapping technique. We used the structural data to identify active photocatalytic sites and their properties before, after, and during the photo-Fenton-like reaction with and without visible light irradiation. We obtained insight into the working state of the catalysts, elucidated the mechanism of the photocatalytic reaction, and identified the role of each active metal site in the photocatalytic process. The final goal was to determine the structure-property-activity relationship of the metal cations in order to optimise the catalyst for the targeted photo-Fenton-like catalytic reaction.

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Application of time-resolved and pulse EPR spectroscopy in the study of mixed valence arylamines for hybrid/organic solar cells (P-101)

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[2]Institute of Nanotechnology (CNR-NANOTEC), Lecce, Italy
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Organic mixed valence systems (MV) are molecules containing two or more redox centers linked by a π-conjugated system, the poly-arylamine MV being the most used. Their structures and electronic properties make them efficient materials for the use as hole transport materials (HTM) in dye-sensitized solar cells (DSSC), OLED and perovskite-based solar cells (PSC). [1,2,3]

This work focuses on the investigation, both in liquid and solid state, of the photophysics of the excited triplet states and on the intramolecular charge transfer in the radical cations of several newly developed arylamine MV.

The paramagnetic nature of both triplet states and radical cations makes EPR spectroscopy a particularly useful technique to carry out their characterization.

In particular, Time-resolved EPR spectroscopy is employed to investigate the photophysics of the excited triplet states and rationalize their population and depopulation mechanisms, while echo-detected and hyperfine EPR techniques are employed to obtain information on the spin localization and charge dynamics in the radical cations and on intramolecular charge transfer interactions in solid state.

The aim of this study is to better understand the photophysical and photochemical properties of these promising molecules that can be deployed in a variety of organic optoelectronic devices.

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Characterization of triplet vinylidenes (P-102)

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Singlet vinylidenes have been proposed as intermediates in a series of organic reactions, and very few were studied by matrix isolation or gas-phase spectroscopy. However, triplet vinylidenes, featuring two unpaired electrons at a monosubstituted carbon atom, had only been predicted as electronically excited-state species until our group's report on the first ground-state triplet vinylidene [1].

One likely reason for the lack of experimental data on ground-state triplet vinylidenes was the missing synthetic access. The successful synthesis of stable diazoalkenes ($R_2C=C=N_2$), which have been predicted to be the best vinylidene precursors [2], enabled entry into this new fundamental compound class.

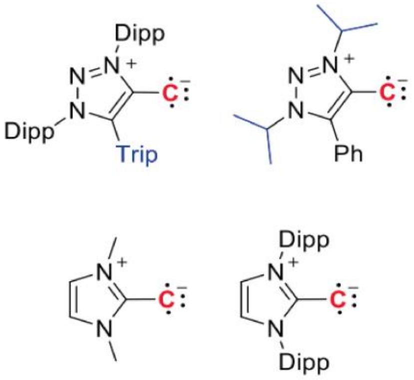

Figure 1: The new diazoalkane precursors. These precursors differ in both the heterocycle structure and ring substituent groups from the previously

Following the discovery of triplet vinylidene, we started working on fine-tuning vinylidene properties such as reactivity and stability. To this end, a series of diazoalkene precursors (Figure 1), differing in the heterocycle structure and ring substituent groups, is photolyzed to produce triplet species. Here, I will show the generation of the triplet species via free induction decay (FID) and continuous wave (cw) experiments at Q- and X-band, respectively. Additionally, temperature-dependent EPR measurements are carried out to conclude whether the generated radicals are in triplet ground-state via the Curie-Weiss plots. In the future, we will employ orientation-selective ENDOR experiments with vinylidenes ^{13}C labelled at the terminal carbon to determine the ^{13}C hyperfine interaction tensor for the various structures. Our results will establish a_{iso} as a spectroscopic signature of triplet vinylinedes.

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Investigation of the phototautomerism process in a free-base porphyrin using advanced EPR and optical techniques (P-103)

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Phototautomerism in the excited states of free-base 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin ($H_2TPPS_4^-$) has been investigated combining, for the first time, advanced Electron Paramagnetic Resonance (EPR) with fluorescence spectroscopy. Time Resolved EPR (TR-EPR) spectroscopy, performed in protic and deuterated solvents and in the presence of magnetophotoselection (MPS), confirms the occurrence of phototautomerization and additionally suggests the formation of the cis tautomer as a minor component. The zero-field splitting parameters and triplet sublevel populations along with fluorescence anisotropy results indicate that the process is slow both in the excited singlet and triplet states. The results obtained by TR-EPR with MPS, and fluorescence anisotropy have been interpreted within a model which considers four quasi-degenerate states to describe the first excited state of the porphyrin and a fast trans-trans tautomerization promoted by a spin-vibronic coupling mechanism for intersystem crossing [1,2].

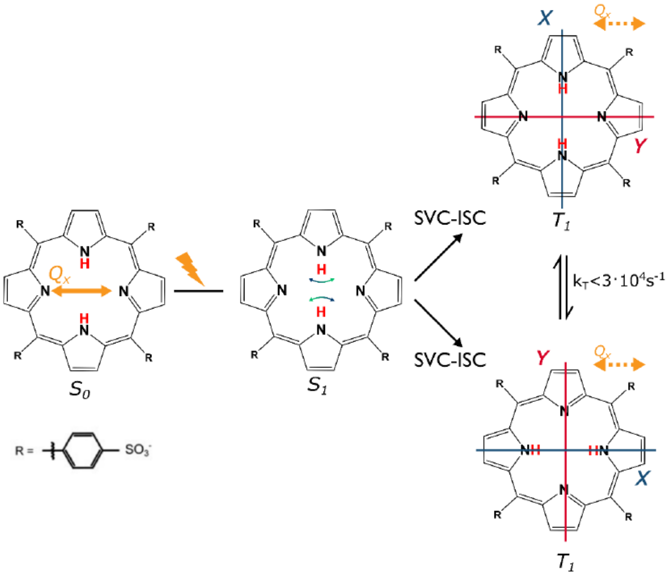

Figure 1*: Proposed scheme for phototautomerism in free-base* $H_2TPPS_4^-$

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[1] Völker, S.; Van Der Waals, J. H. *Mol. Phys.* **1976**, *32* (6), 1703–1718.
[2] Lopes, J. M. S.; *et al. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* ***2019****, 209, 274–279.*

Asymmetric Counteranion Directed Photoredox Catalysis (P-104)

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Although photocatalysts have very widespread applications, controlling their selectivity is the greatest challenge. We found a potentially general solution for radical cation based asymmetric photoredox catalysis. We show that organic salts with constrained imidodiphosphorimidate counteranions catalyze highly enantioselective [2+2] cross-cycloadditions of styrenes. For this investigation, EPR played a very important role in deducing key information about the reaction mechanism. EPR study demonstrated the life-time of the catalysis for photocatalyst 4e at -83 °C and at -173 °C. EPR was also crucial in the verification of the dependence of the light intensity to the photocatalysis of photocatalyst 4e. Systematic EPR investigations showed the effect of the individual components (solvent, reactants **1a** and **1b**, naphthalene, photocatalyst **4e**) under blue light irradiation to the reaction. These studies confirmed that only the presence of the catalyst results in a photocatalyst reaction by the observation of an isotropic and fast doublet radical electron spin coupling only after a complete reaction mixing. EPR also aided in identifying the origin of the seven hyperfine splitting observed for the N-Ph-acridinium photocatalyst 5e is due to the N-Ph moiety[1].

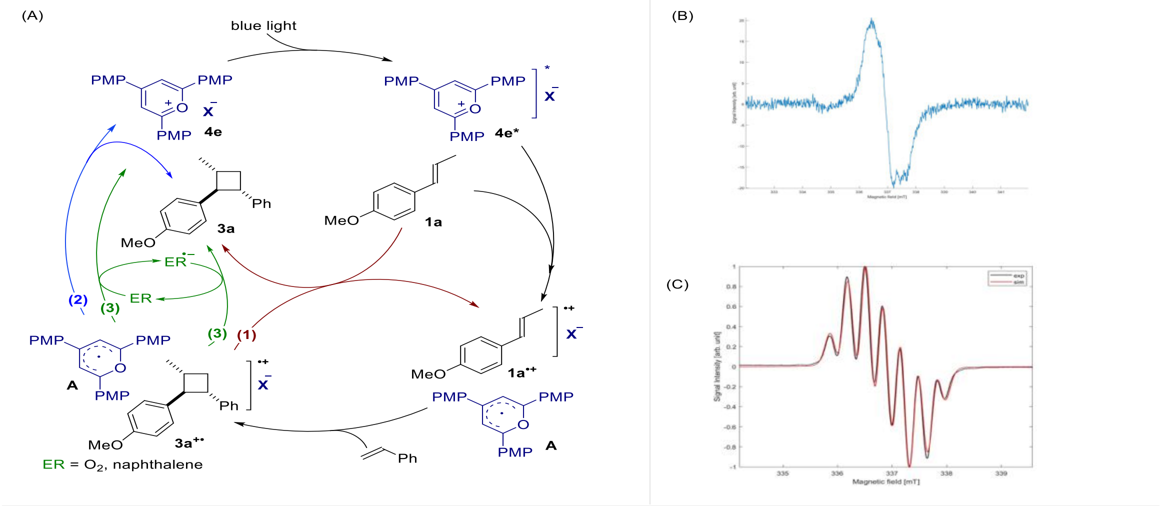

Figure 1*:* (A) Proposed catalytic cycle. (B) EPR measurements of the reaction using 4e at – °C and (C) EPR measurements of the reaction mixture using photocatalyst e at – 0 °C under continuous photoexcitation with blue light[1].

References:

[1] Das, S., Zhu, C., Demirbas, D., Bill, E., De, C. K., & List, B. (2023). Asymmetric counteranion-directed photoredox catalysis. Science. https://doi.org/ade8190

Electric Manipulation of the Dipolar Interaction of the Photoinduced Electron-hole Pair in a Charge-Transfer Molecule (P-105)

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The interplay between the electric and magnetic degrees of freedom in paramagnetic materials has been studied due to the promise of locally manipulating electron spins, potentially contributing to the field of quantum computation [1]. Among different molecular magnets, charge-transfer (CT) molecules have been proposed as suitable qubit candidates, given they can be optically initialised in well-defined states and their structural tunability [2]. In this study, we report the spin-electric coupling (SEC) of the CT state in an ensemble of 10-phenyl-10 ,1 0′ -spiro[acridine- , ′-anthracen]-10′-one (ACRSA). The magnetic anisotropy of the CT state is correlated to the separation and, therefore, the electric dipole moment of the photoinduced electron-hole pair in the molecule. Hence, such state may exhibit a SEC. A modified Hahn-echo sequence [Figure 1(a)] is employed to investigate the SEC by monitoring the EPR intensity while varying the electric-field pulse. A coherent modulation to the echo (similar to [1]) is observed, confirming the presence of the SEC in ACRSA. The reported electric-field sensitivity can be explained by the interaction between the electric field and the electron-hole-pair's dipolar coupling. These findings bring us closer to implementing quantum control by electrically manipulating spins.

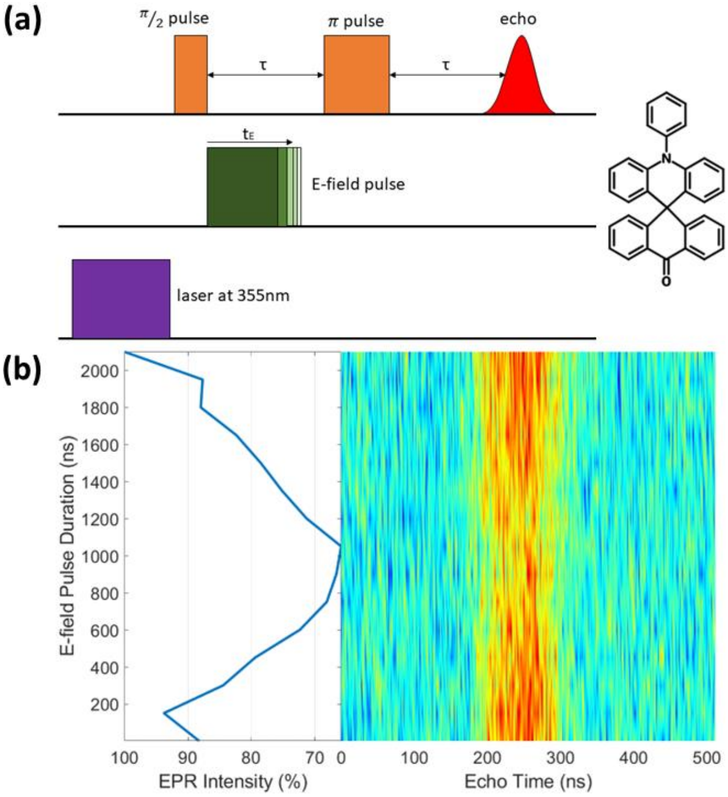

***Figure 1**: (a) Modified Hahn echo sequence used for probing SEC, including an initial laser pulse and an electric-field pulse. Inset: structure of the ACSRA molecule.*
(b)The electric-field pulse induces a spin-packet phase shift, resulting in a modulated echo intensity

[1] J. Liu et al., Nature Physics **2021**, 17, 1205-1209
[2] H. Mao et al., J. Phys. Chem. Lett. **2021**, 12, 2213-2218

Luminescent organic radicals with high-spin excited states (P-106)

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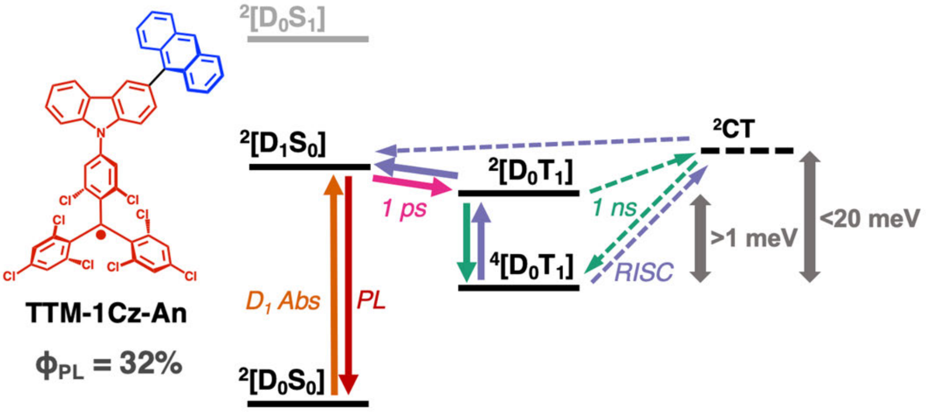

***Figure 1**: Molecular structure, emission quantum yield (ϕ_{PL}) and state diagram of a luminescent radical-acene dyad. Temperature-activated reverse intersystem crossing (RISC) from the strongly exchange coupled quartet state enables efficient emission from the radical excited state.*

Robust spin-optical interfaces are key to harnessing the quantum resources of materials.[1] However, radical-chromophore dyads have been non-luminescent to date.[2]

Here I will present the first organic molecules displaying both efficient luminescence and a high yield of high-spin multiplicity excited states. This is achieved by designing an energy resonance between the emissive doublet and triplet energy levels, here on tris(2,4,6-trichlorophenyl) methyl-carbazole radicals[3] covalently linked to anthracene. The doublet photoexcitation delocalises onto the acene within a few picoseconds and subsequently evolves to a pure quartet (S = 3/2) state of mixed radical-triplet character near 1.8 eV. These high-spin states are coherently addressable with microwaves even at 295 K in the solid state, with optical read-out enabled by intersystem crossing to emissive states as demonstrated by optically detected magnatic resonance (ODMR).

This mechanism simultaneously supports a high efficiency of initialisation, spin manipulations and light-based read-out at room temperature.[4] The integration of luminescence and high-spin states creates an organic materials platform for emerging quantum technologies.

References:

[1] Awschalom *et al.*, *Nat. Photonics* **12**, 516-427 (2018).
[2] Quintes *et al.*, *Nat. Rev. Chem.* **7**, 75–90 (2023).
[3] Ai *et al.*, *Nature* **563**, 536–540 (2018).
[4] Gorgon *et al.*, https://arxiv.org/abs/2303.13934

Spin communication between light-induced triplet state and stable radical in different chromophore–radical systems (P-107)

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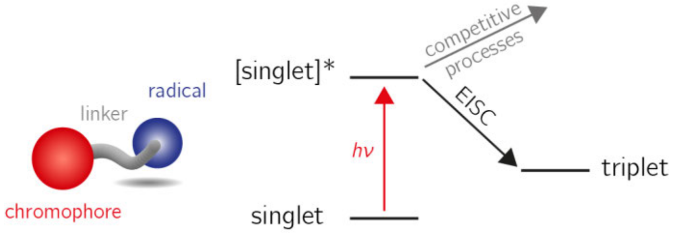

***Figure 8**: Through light excitation of the chromophore the excited singlet state is formed. Subsequently, the triplet state can be generated by enhanced intersystem crossing (EISC).*

To identify novel materials for applications in molecular spintronics, a deeper understanding of the spin-spin interactions and their manipulation is crucial. To achieve this, we investigate molecular triplet-doublet systems which provide the advantage of systematic structural modifications [1,2]. They typically consist of a chromophore covalently linked to a radical. In such systems, the triplet state of the chromophore is accessible by light excitation via enhanced intersystem crossing (EISC). Following triplet formation, the magnitude of the exchange interaction between the two spin centres dictates the mechanism by which they interact [3].

We use optical spectroscopic techniques, such as femtosecond UV-vis transient absorption spectroscopy to observe the differences in the ultrafast photochemical behaviour. To study the magnetic interactions between the two spin centres, we use transient EPR techniques. This work compares various chromophores, such as perylene diimides (PDIs) and boron-dipyrromethene (BODIPYs), attached via different linkers to nitroxide or trityl radicals with respect to the kinetics of the different photochemical processes, triplet formation yields and magnetic properties. In molecular systems with trityl as the stable radical, energy transfer between the excited chromophore and the radical limits the triplet yield. The length of the linker is shown to influence the rate and yield of the processes observed following light excitation as well as the nature of the interaction. These observations finally lead us to propose design guidelines for molecular systems comprising chromophores in which higher excited states can be efficiently sensitised in proximity of an unpaired electron spin.

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[2] T. Quintes, M. Mayländer, S. Richert *Nat. Rev. Chem.* **2023**, *7*, 75–90.
[3] M. Mayländer, S. Chen, E. R. Lorenzo, M. R. Wasielewski, S. Richert *J. Am. Chem. Soc.* **2021**, *143*, 7050–7058.

Direct comparison of Light Induced Triplet-Triplet Electron Resonance (LITTER) spectroscopy with Förster Resonance Energy Transfer (FRET) (P-108)

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We present a direct comparison of light induced triplet-triplet electron resonance (LITTER) spectroscopy[1] with Förster resonance energy transfer (FRET)[2] in two peptide-chain systems of known length, augmented with different chromophore pairs.

The exemplar systems utilised Zn-substituted tetraphenylporphyrin (ZnTPP) and tetraphenylporphyrin (TPP) ([1]), as well as TPP and erythrosine B (EB) ([2]).

The inter-chromophore distances obtained from LITTER and FRET experiments are in very good agreement, with FRET giving distance ranges of 21.7-31.8 Å for system [1] and 20.5-29.2 Å in system [2]. The corresponding LITTER distance distributions centred on 23 and 25 Å respectively.

1 A. Bertran, et al., *Journal of Physical Chemistry Letters*, 2021, **12**, 80–85.
2 T. Heyduk, *Curr Opin Biotechnol*, 2002, **13**, 292–296.

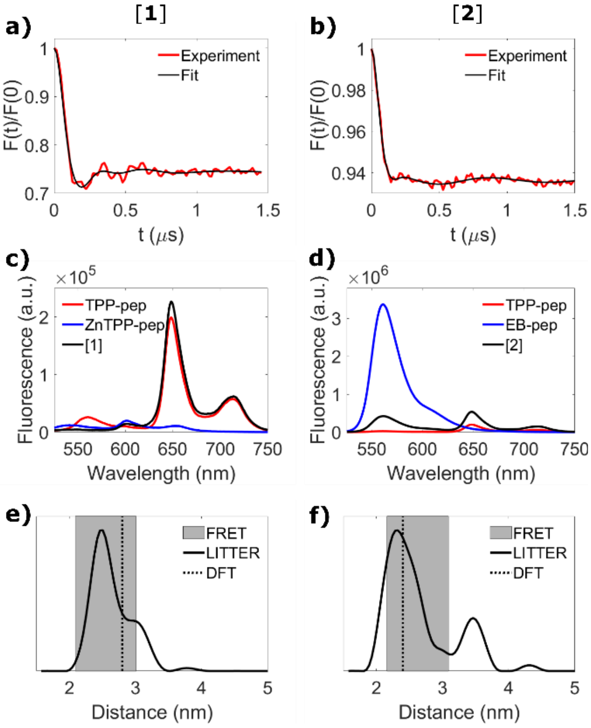

*Figure 9 - (a, b): 2-colour LITTER traces of 40 μM [**1**] (512/556 nm) and 40 μM [**2**] (512/532 nm) (red), respectively, with fits obtained by Tikhonov regularization (black). (c, d): Fluorescence spectra of [**1**] (c) and [**2**] (d) (black), and of mono-labelled TPP-peptide [**3**] (red), ZnTPP-peptide [**4**] (c, blue) and EB-peptide [**5**] (d, blue). Excitation was performed at 510 nm. (e, f) The determined distances for [**1**] (e) and [**2**] (f) by FRET (grey), LITTER (solid line) and DFT (dotted line). FRET analysis was carried out at 561nm.*

Influence of the substitution position on spin communication in light-induced multi-spin systems (P-109)

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Molecular assemblies consisting of a chromophore and a stable radical may form versatile multi-spin systems upon photoexcitation.[1,2] Because of their modular nature, these molecules are excellent candidates for the investigation of structural influences on spin communication properties.[1]
Within this study, we investigate multiple perylene–nitroxides and their bromo-perylene analogues, whereby the radical or bromine atom is connected to different positions of the perylene core (see Fig. 1).

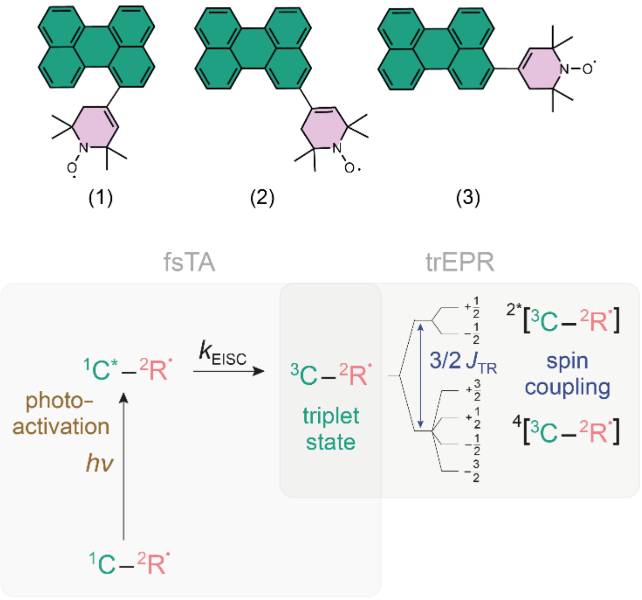

Figure 1: *Structures of the investigated perylene-nitroxides (top) and simplified Jablonski diagram of a modular chromophore (C) – radical (R) system (bottom).*

The multi-spin systems are investigated using theoretical methods, with the exchange interaction parameter (J_{TR}) being the crucial parameter regarding spin communication.[3] The experimental investigation is carried out using transient electron paramagnetic resonance (trEPR) spectroscopy to characterize the spin species as well as optical techniques, including femtosecond transient absorption (fsTA) spectroscopy, to investigate the excited state dynamics and evaluate the triplet yield (Φ_{T}).

Based on theoretical investigations, the sign and magnitude of J_{TR} varies depending on the substitution position. fsTA investigations demonstrate differences in the excited singlet state lifetimes and Φ_{T}. trEPR spectra suggest differences in the exchange interaction although quartet state formation is observed for all the investigated perylene-nitroxides.

References:

[1] T. Quintes et al., *Nature Reviews Chemistry* **2023**, *7*, 75–90
[2] M. Mayländer et al., *Journal of the American Chemical Society* **2021**, *143*, 7050–7058
[3] M. Franz et al., *Chemical Science* **2022**, *13*, 12358–12366

Synthesis of Perylene-bis(Trityl) Systems And Their Characterization in the Dark State (P-110)

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To generate well defined initial spin states suitable for applications in quantum information science, photo generated multi-spin systems are of great interest due to their long coherence times.[1,2] Furthermore, the use of organic radicals facilitates the tuning of the desired chemical and spin properties. Thus, two novel covalently linked perylene-bis(trityl) systems were synthesized and characterized via EPR spectroscopy to get a better understanding about the electron interaction in the dark state via cw-EPR spectroscopy and pulsed dipolar EPR spectroscopy, in particular Double Quantum Coherence (DQC) EPR. For the shorter bridged system, a small exchange coupling of -0.5 MHz was observed and both systems exhibit orientation selectivity in the DQC time traces.

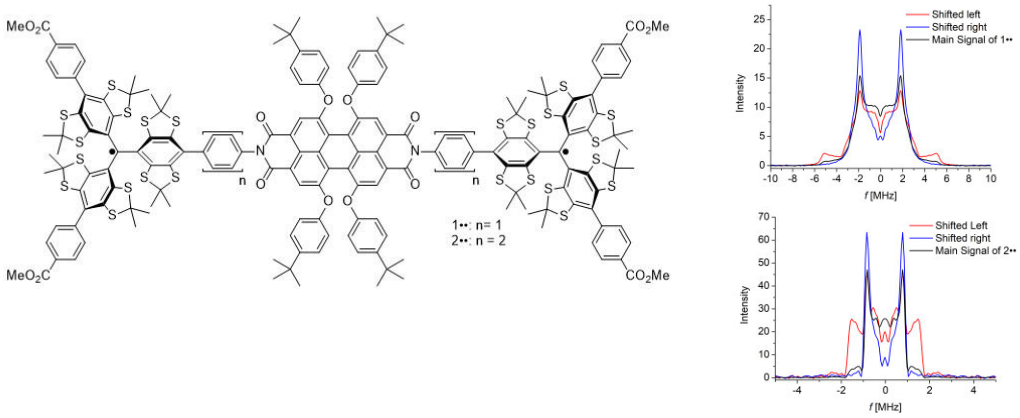

***Figure 1**: (left) Structure of the investigated Perylene Bis(Trityl) systems. (right) Orientation selectivity observed in the Pake pattern of the DQC time traces.*

References:
[1] T. Quintes, M.Mayländer, S. Richert, *Nat. Rev. Chem.* **2023**, 1-16.
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