

## Generating and enhancing spin-light interfaces in molecular qubits

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Spins in molecules provide a platform for quantum information science which can deploy the versatility of synthetic chemistry. In particular, molecular ground-state electronic spins which can be interfaced with light are attractive as quantum bits (qubits). Such systems could combine key features of semiconductor spin qubits—e.g., single-spin detection and high-fidelity coherent control—with the versatility afforded by a molecular architecture, and therefore open up tailor-made qubits for applications such as nanoscale quantum sensing.

Here we outline our work to generate optical interfaces for ground-state molecular spins. Using Cr(IV)-based molecules, we show how core functionality of semiconductor spin qubits—optical initialization, optical read out, and coherent microwave control—can be realised in a molecular architecture [1]. We then outline two distinct ways in which the spin coherence of these optically addressable molecular qubits can be enhanced via control over the qubit’s symmetry: (*i*) modifying the ligands co-ordinating the qubit, and (*ii*) modifying the qubit’s host matrix [2]. These modifications induce magnetic-field insensitive spin transitions (clock transitions) which enhance coherence, and we model this behaviour from first principles across a series of molecules using cluster-correlation expansion methods. Finally, we show how host-matrix control can enhance other key qubit properties including optical spin initialisation and read out fidelities, and spin-lattice relaxation times.

Overall, these results demonstrate how core qubit properties of optical initialization, optical read out and coherent control can be realised in ground-state molecular spins, how the portability and tunability of molecular systems can be used to enhance qubit properties, and highlight opportunities for quantum sensing with optically active molecular spins.

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### References

- [1] S. L. Bayliss\*, D. W. Laorenza\*, P. J. Mintun, B. D. Kovos, D. E. Freedman, D. D. Awschalom, *Science* **370**, 1309 (2020)
- [2] S. L. Bayliss\*, P. Deb\*, D. W. Laorenza\*, M. Onizhuk, G. Galli, D. E. Freedman, D. D. Awschalom, arXiv:2204.00168 (2022)

# Probing Charging and Discharging of Organic Radical Batteries by EPR

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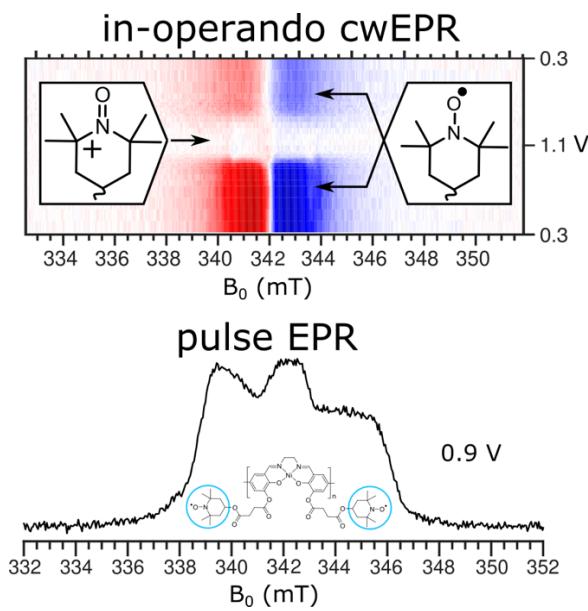
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Electron spins are unique local probes for elucidating redox reactions associated with the operation of organic radical batteries (ORBs). EPR spectroscopy can thus be employed to study charging and discharging processes in this promising class of electrochemical power sources based on organic radicals as redox-active groups.

Here we report on the development of a versatile on-substrate electrode setup for spectroelectrochemical EPR measurements on redox conductive polymers for ORBs [1]. Quantitative in-operando EPR experiments performed on electrochemical cells with a di-TEMPO Ni-Salen polymer as active electrode material demonstrate a strong decrease in the number of paramagnetic centres upon oxidising the film [2]. The distinct EPR signatures of the TEMPO-containing polymer and its fragments in different molecular environments are used to study its degradation upon repeated cycling. A comparison between the number of EPR-active sites and the number of electrochemically active charges, as measured by cyclic voltammetry, provides information on the nature of the degradation process.

Low-temperature ex-situ pulse EPR measurements on the oxidised polymer film reveal the spectrum of dilute nitroxide species, which may be associated with electrochemically inactive islands. These experiments pave the way for advanced EPR techniques for accurately determining distances between adjacent paramagnetic centres and thus for identifying performance-limiting loss mechanisms, which can eventually help develop strategies for making ORBs powerful contenders on the path towards sustainable electrochemical power sources.



## References

- [1] I. Kulikov, N. A. Panjwani, A. A. Vereshchagin, D. Spallek, D. A. Lukianov, E. A. Alekseeva, O. V. Levin, J. Behrends, *ChemRxiv*, DOI: 10.26434/chemrxiv-2022-zctv6 (2022)
- [2] A. A. Vereshchagin, D. A. Lukyanov, I. R. Kulikov, N. A. Panjwani, E. A. Alekseeva, J. Behrends, O. V. Levin, *Batteries & Supercaps* **4**, 336 (2021)

## New light-induced Pulsed ESR Dipolar Spectroscopy methodologies for the elucidation of molecular conformation

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The suitability of the photoexcited triplet state of porphyrins for nanometer distance measurements by Pulsed ESR Dipolar Spectroscopy (PDS) was demonstrated in combination with nitroxide radicals. Thanks to its non-Boltzmann population, the photoexcited triplet enhanced signal intensity when used as detection spin in DEER [1] and improved modulation depth when used as pump spin in LaserIMD [2]. Here we exploit the orientation selection effects in these triplet–nitroxide experiments to extract additional conformational information in model peptides with different chromophores, namely tetraphenylporphyrin, diiodo-BODIPY and Erythrosin B (Fig. 1 (a)) [3]. Using simulations and DFT calculations, we extract distance distributions and relative orientations of the two spin-bearing moieties, allowing the dominant conformation of the peptide in frozen solution to be identified. We also present, for the first time, a frequency-correlated version of LaserIMD, which monitors the complete orientation dependence of the system in a single experiment.

Going a step further in light-induced PDS, we present the new technique of Light-Induced Triplet-Triplet Electron Resonance spectroscopy (LITTER) [4], which uses photoexcited triplet states as both detection and pump spins, enabling both the distance and angular distributions between the two triplet moieties to be determined in a model peptide (Fig. 1 (b)). LITTER removes the requirement of current light-induced PDS techniques to have a permanent paramagnetic moiety, becoming more suitable for in-cell applications and potentially giving access to distance determination in unmodified macromolecular systems containing photoexcitable moieties. LITTER also has the potential to enable direct comparison with FRET and combination with microscopy inside cells.

- [1] M. Di Valentin *et al.*, *J. Am. Chem. Soc.* **136**, 6582–6585 (2014).
- [2] C. Hintze *et al.*, *J. Phys. Chem. Lett.* **7**, 2204–2209 (2016).
- [3] A. Bowen *et al.*, *J. Phys. Chem. Lett.* **12**, 3819–3826 (2021).
- [4] A. Bertran *et al.*, *J. Phys. Chem. Lett.* **12**, 80–85 (2021).

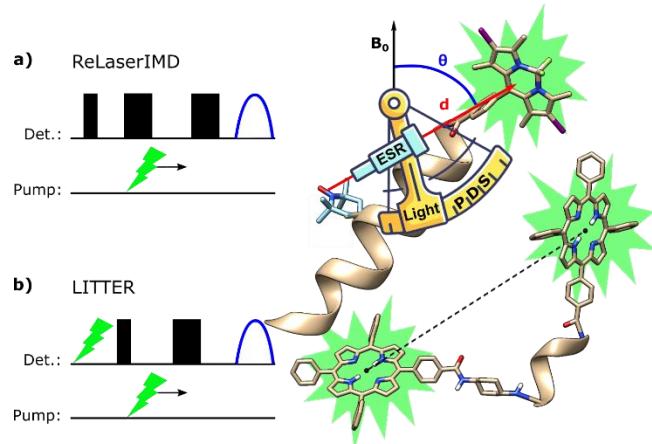


Figure 1. Pulse sequences for the Refocused LaserIMD (a) and LITTER (b) experiments, and structures of model peptides used in the studies of the orientational effects.



# Diamond Based Microwave Quantum Amplifier

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## Abstract

Nitrogen vacancy (NV) color centers in single crystal diamond that are negatively charged ( $\text{NV}^-$ ) are electronic triplets that are known to be optically-polarized to the  $m_s=|0\rangle$  state upon green light irradiation. At large enough static magnetic field (above  $\sim 1\text{k Gauss}$ ) the  $|0\rangle$  state is located above the  $|-1\rangle$  state and thus the optical pumping results in a state of population inversion. This population inversion can in principle be used to amplify microwave radiation that corresponds to the  $|0\rangle \leftrightarrow |1\rangle$  energy difference by stimulated emission (the so-called MASER effect – microwave amplification by stimulate demission of radiation). Such kind of microwave quantum amplifier can prove to be very useful in terms of its noise performance, ultimately enabling even to amplify the signal of single microwave photons in some scenarios. While this possible use of NVs in diamond is well-known, it has never been actually demonstrated in practice, due to various experimental challenges [1]. (A diamond-based MASER *oscillator* was achieved a few years ago [2], but not an amplifier). In this talk I will present our recent experiments in this field, which demonstrate for the first time the operation of diamond-based quantum microwave amplifier, including its design and construction phases, as well as tests of its performance in terms of gain, bandwidth and noise.

[1] Journal of Applied Physics 129, 144503 (2021)

[2] Nature volume 555, pages493–496 (2018)

# Room temperature radical-pair spin relaxation dynamics at low magnetic fields studied by spin-dependent charge carrier recombination currents in organic light-emitting diodes

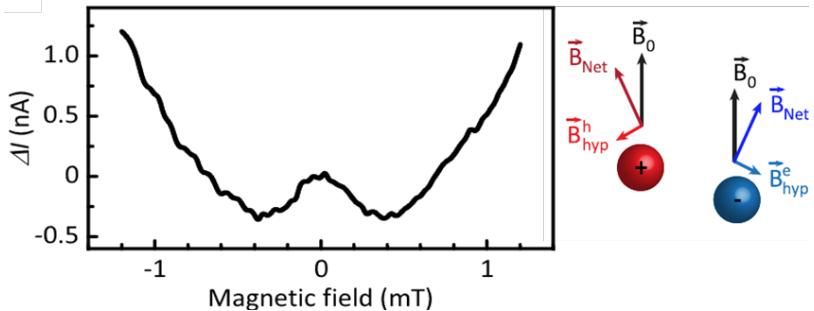
**Christoph Boehme**,<sup>1</sup> Taniya H. Tennahewa,<sup>1</sup> Sanaz Hosseinzadeh,<sup>1</sup> Sebastian I. Atwood,<sup>1</sup> Henna Popli,<sup>1</sup> Hans Malissa,<sup>1,2</sup> and John M. Lupton<sup>1,2</sup>

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We have experimentally tested the hypothesis that the strong magnetic field dependence of radical-pair-like processes is related to a strong magnetic field dependence of spin-relaxation times when an applied magnetic field competes in magnitude with internal, proton-hyperfine induced magnetic fields. Electric current in bipolar (electron/hole) injector devices, essentially organic light-emitting diodes (OLEDs) under forward bias, provides straightforward experimental access to spin-dependent charge carrier recombination rates, which have been known to be qualitative analogues to spin-dependent radical pair reaction rates<sup>1</sup>. We used such spin-dependent electric currents to observe pulsed electrically detected magnetic resonance, specifically electrically detected Hahn-echoes<sup>2</sup> for the measurement of charge carrier spin coherence times  $T_2$ ; and electrically detected inversion recovery<sup>2</sup> for the measurement of longitudinal charge carrier spin relaxation times  $T_1$ . These measurements were performed in a regime, where the static magnetic field ( $B_0$ ) is so small that magnetic polarization is negligible ( $1 \text{ mT} \lesssim B_0 \lesssim 8 \text{ mT}$ )<sup>3</sup>.

The experiments required arbitrary waveform generation (AWG) for the direct synthesis of the RF pulse sequences needed for coherent spin-control. The results of this study have revealed a strong magnetic-field dependence of  $T_1$  at magnetic field strengths where radical-pair processes, e.g. magnetoresistance, are particularly magnetosensitive. In conclusion, we see that when  $B_0$  becomes so small that it is essentially cancelled by the randomly oriented hyperfine fields within the thin-film material, the individual spin pairs lose their well-defined quantization axis and a  $T_1$  process is not well-defined anymore<sup>3</sup>. Measurements of  $T_1$ , therefore, reveal values that are strongly quenched, converging towards the value of  $T_2$ .



*Room temperature current change in an OLED based on the  $\pi$ -conjugated co-polymer SY-PPV, under forward bias conditions, as a function of an applied mT-range magnetic field. The sketch illustrates how an externally applied magnetic field and locally varying hyperfine field components add up to the net magnetic field that acts upon individual charge carriers. When these net fields are dominated by  $B_0$ , a well-defined identical quantization axis will exist for all charge carrier spin pairs within the polymer film.*

This work is supported by the Department of Energy DE-SC0000909.

- [1] T. Grünbaum et al., *Faraday Discuss.* **221**, 92 (2020).
- [2] W. J. Baker et al., *Phys. Rev. Lett.* **108**, 267601 (2012).
- [3] T. H. Tennahewa et al., arXiv:2207.07086 [cond-mat.mes-hall] (2022).

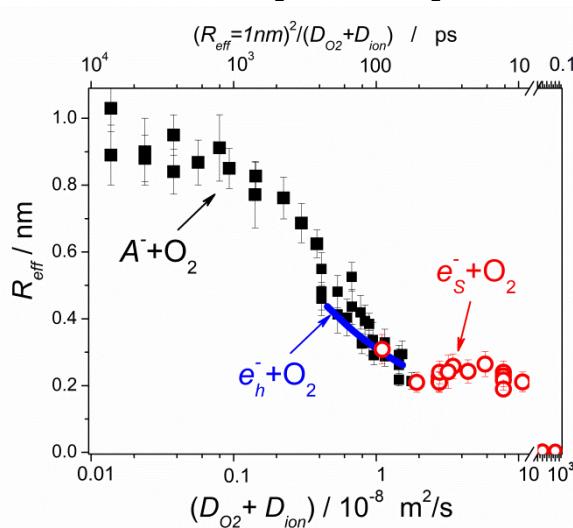
# Spin-selective reactions in three-spin systems in high-energy radiation experiments

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The spin-correlated radical pair is a basic object of spin chemistry that is thoroughly studied by many researchers. The next important step is to understand 3-, 4-, ...-spin systems. Constructing covalently bonded multi-spin structures is a promising strategy. This approach, however, is of interest primarily from a quantum computing perspective since the complexity of such structures takes away the possibility to study spin effects in elementary spin-selective chemical reactions involving free small paramagnetic particles, such as solvated electrons, radicals, oxygen molecule, etc. The purpose of this lecture is to draw community's attention to possibilities of studying 3-spin systems using the high-energy radiation, which, in a solution containing paramagnetic scavengers, creates an ensemble of three-spin systems "spin-correlated radical ion pair/ paramagnetic particle" composed of individual species.

The lecture focuses on a particular example of a very important spin-selective reaction of electron transfer to molecular oxygen in its triplet ground state



**Figure 1.** Effective radii  $R_{\text{eff}}$  of i) electron scavenging by  $\text{O}_2$  in alkanes (circles) and water (line, data from [3]); ii) of electron transfer to  $\text{O}_2$  from aromatic radical anions in various alkanes (squares) on the reactants' relative diffusion coefficient. The upper scale shows a typical time scale for the diffusion controlled encounters.

time for triplet  $\text{O}_2$ , that is about of 8 ps [2]. As the factors reducing the intersystem crossing rate in the encounter complex, the Heisenberg spin exchange interaction and the quantum Zeno effect are discussed.

[1] V. I. Borovkov et al., J. Phys. Chem. A **117**, 1692(2013)

[2] C.-L. Teng et al., J. Magn. Reson. **148**, 31 (2001)

[3] A. J. Elliot, Radiat. Phys. Chem. **34**, 753 (1989)

## **EPR Study of charge transfer co-crystals of DBTTF:F4TCNQ**

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Charge transfer crystals exhibit unique electronic and magnetic properties with interesting applications. The charge transfer single crystal formed by dibenzotetrathiafulvalene (DBTTF) together with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) presents a long-range ordered supramolecular structure of segregated stacks, with a unitary degree of charge transfer. Thus, the crystal structure is composed of dimerized radical molecules with unpaired electrons. EPR temperature studies of polycrystalline sample revealed that oxidation reduction reaction doesn't occur between every two neighboring molecules but upon charge transfer the electron migrate through the stack from 18.6 Å at 5 K up to 19.42 Å at 300 K. Between 100 to 150 K we observed the shortest distances of 17-16.87 Å suggesting a glass transition behavior in this temperature range.

## Molecular spin qudits: a promising ingredient for quantum technologies

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The potential to solve problems with large impact on science, society and economy makes the realization of quantum computers one of the hottest topics in current research. However, to deal with problems intractable on classical device, each logical unit must suppress unavoidable errors via quantum error correction. The actual realization of this goal is still far even for the most advanced architectures, based on superconducting qubits or ion traps. In this respect, molecular nanomagnets (MNMs) offer a very promising alternative, opening a new route towards a scalable quantum computer. These magnetic molecules are characterized by a sizeable number of accessible low-energy states that can be coherently manipulated by microwave and radiofrequency pulses, thus opening the possibility use them as molecular qudits.

In my presentation, I review some recent results on molecular qudits/qubits. In particular, I show that MNMs can be exploited to define qubits with embedded quantum error correction in single molecules [1-3], thus circumventing the large overhead in the number of physical units required by standard quantum error correction codes. Moreover, I show that molecular qudits can improve the potential for quantum simulations [4]. Then, I briefly report the characterization of promising molecular qudits using broadband NMR [5] and discuss some recent results on the study of the two main sources of decoherence in MNMs, i.e., interactions with nuclear spins and phonons [6,7].

Finally, I will show how chiral-induced spin selectivity could be harnessed as a useful tool to spin-polarize molecular qubits, thus potentially raising their operating temperature [8].

- [1] A. Chiesa, E. Macaluso, F. Petiziol, S. Wimberger, P. Santini, and S. Carretta, J. Phys. Chem. Lett. **11**, 8610 (2020).
- [2] E. Macaluso, M. Rubín, D. Aguilà, A. Chiesa, J. I. M. L. A. Barrios, P. J. Alonso, O. Roubeau, F. Luis, G. Aromí, and S. Carretta, Chem. Sci. **11**, 10337 (2020).
- [3] A. Chiesa, F. Petiziol, M. Chizzini, P. Santini and S. Carretta, in preparation
- [4] F. Petiziol, A. Chiesa, S. Wimberger, P. Santini and S. Carretta, npj Quantum Inf. **7**, 133 (2021).
- [5] E. Garlatti, L. Tesi, A. Lunghi, M. Atzori, D. J. Voneshen, P. Santini, S. Sanvito, T. Guidi, R. Sessoli, S. Carretta, Nature Commun. **11**, 1751 (2020).
- [6] F. Tacchino, A. Chiesa, R. Sessoli, I. Tavernelli, S. Carretta, Molecular spin qudit for simulation of light-matter interaction, J. Mater. Chem. C **9**, 10266 (2021).
- [7] S. Chicco, A. Chiesa, G. Allodi, E. Garlatti, M. Atzori, L. Sorace, R. De Renzi, R. Sessoli and S. Carretta, Chem. Sci. **12**, 12046 (2021).
- [8] A. Chiesa, M. Chizzini, E. Garlatti, E. Salvadori, F. Tacchino, P. Santini, I. Tavernelli, R. Bittl, M. Chiesa, R. Sessoli, and S. Carretta, J. Phys. Chem. Lett. **12**, 6341-6347 (2021)

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# Light-induced Pulsed Dipolar EPR Spectroscopy for distance and orientation analysis

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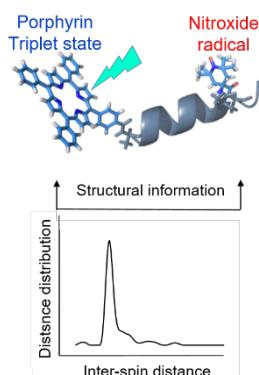
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EPR pulsed dipolar spectroscopy is a well-established technique to determine precise distance distributions between paramagnetic centers with distances ranging from around 1.6 nm up to 16 nm. In combination with site-directed spin labeling, it is ideally suited for structural characterizations of macromolecules and complexes, and has emerged as valuable tool in structural biology.

In recent years, porphyrins have been introduced in the selection of spin labels for dipolar spectroscopy applications. In their ground state, these chromophores are diamagnetic and thus EPR-silent, but, upon laser photoexcitation, their triplet state can be populated via intersystem crossing from the lowest excited singlet state, generating in this way the paramagnetic center.

Here we present various light-induced techniques, which exploit the distinctive properties of the porphyrin triplet state including the electron spin polarization. In combination with nitroxide spin labels or using two porphyrin probes, they enable both the distance and angular distributions between the two paramagnetic moieties to be determined. Pulsed dipolar spectroscopy has been applied on peptide-based spectroscopic rulers in order to test the accuracy, sensitivity and distance limits and it has been extended to paradigmatic proteins, containing an endogenous porphyrin probe.<sup>1-4</sup> Different chromophores with high triplet yield have also been introduced and the hyperpolarization of the nitroxide radical has been considered for a further increase in sensitivity.<sup>5</sup>

The methodology has a high potential for measuring nanometer distances in more complex biological systems and for future in-cell applications.



## References

1. M. Di Valentin, M. Albertini, E. Zurlo, M. Gobbo and D. Carbonera, *J. Am. Chem. Soc.* 136 (2014) 6582-6585
2. M.G. Dal Farra, S. Richert, C. Martin, C. Larminie, M. Gobbo, E. Bergantino, C.R. Timmel, A. M. Bowen, M. Di Valentin *ChemPhysChem* 20 (2019) 1-6
3. A. Bertran, K. B. Henbest, M. De Zotti, M. Gobbo, C. R. Timmel, M. Di Valentin, A. M. Bowen, Light-Induced Triplet-Triplet Electron Resonance Spectroscopy. *J. Phys. Chem. Lett.* 12 (2021) 80-85
4. A. M. Bowen, A. Bertran, K. B. Henbest, M. Gobbo, C. R. Timmel, M. Di Valentin, Orientation-Selective and Frequency-Correlated Light-Induced Pulsed Dipolar Spectroscopy. *J. Phys. Chem. Lett.* 12 (2021) 3819-3826
5. M.G. Dal Farra, C. Martin, E. Bergantino, Y.E. Kand rashkin, A. van der Est, M. Di Valentin, Electron spin polarization transfer induced by triplet–radical interactions in the weakly coupled regime. *Phys. Chem. Chem. Phys.* 22 (2020) 19982-19991

# Spin-Spin Interactions and their Impact on Organic Light-Emitting Devices

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Spin-spin interactions in organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) are pivotal because radiative recombination is largely determined by triplet-to-singlet conversion, also called reverse intersystem crossing (RISC). To explore the underlying process, we apply a spin-resonance spectral hole-burning technique to probe electroluminescence. We find that the triplet exciplex states in OLEDs are highly spin-polarized and show that these states can be decoupled from the heterogeneous nuclear environment as a source of spin dephasing and can even be coherently manipulated on a spin-spin relaxation time scale  $T_2^*$  of 30 ns. Crucially, we obtain the characteristic triplet exciplex spin-lattice relaxation time  $T_1$  in the range of 50  $\mu$ s, which far exceeds the RISC time. We conclude that slow spin relaxation rather than RISC is an efficiency-limiting step for intermolecular donor:acceptor systems. Finding TADF emitters with faster spin relaxation will benefit this type of TADF OLEDs. [1].

## References

- [1] S. Weissenseel *et al.*, *Science Adv.* **7**, abj9961 (2021).

## **Singlet, doublet and triplet spin control in organic semiconductors**

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The spin of ground and excited state levels in organic semiconductors gives the playground for photophysics in optoelectronics: with applications from solar cells to light-emitting diodes (LEDs) using energy and charge transfer processes.

Spin controls the functional behaviour: where the longstanding issue in organic LEDs is 1:3 ratio of singlet and triplet excitons formed following charge recombination. Non-emissive triplet excitons generated in these device limit the electroluminescence efficiency and the leading methods to recover efficiency is conversion to emissive singlet excitons in thermally activated delayed fluorescence. I discuss optical spectroscopy and magnetic resonance studies that probe key singlet-triplet spin conversion mechanisms in a series of delayed fluorescence emitters with varying energy gaps between the functional exciton states for advancing this technology.[1]

Finally I will present studies on light emission from luminescent organic radicals and the doublet-spin energy manifold.[2] I will discuss why most  $\pi$ -radical systems have poor optical properties, and how we can increase the absorption and luminescence yields with design rules for the chemistry and colour of radical emitters.[3] I will also share new device strategies for OLEDs arising from the singly occupied molecular orbital (SOMO) and doublet-spin properties, resulting in the most efficient performance in the red to infrared wavelength range. This presents a platform for next-generation technologies using spin control from singlet, doublet and triplet excitons.[4]

### **References**

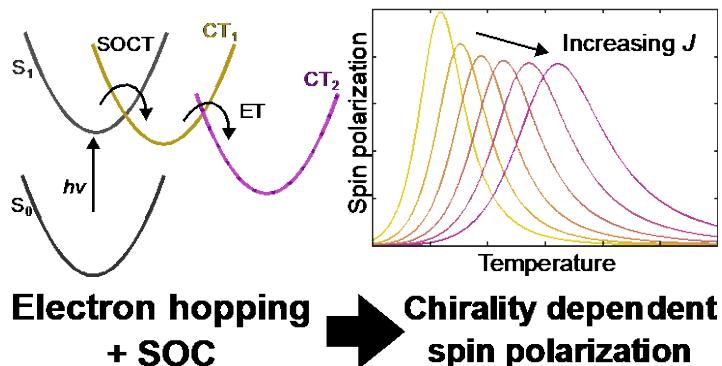
- [1] B. Drummond *et al.*, *Nature Communications*, **12**, 4532 (2021)
- [2] X. Ai *et al.*, *Nature*, **563**, pp. 536–540 (2018).
- [3] Abdurahman *et al.*, *Nature Materials*, **19**, pp. 1224-1229 (2020)
- [4] Li *et al.*, *Nature Communications*, in press (2022)

## Chirality induced spin effects in molecular electron transport

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In this talk I will describe how chirality affects spin transport in molecular systems. In particular I will outline a mechanism by which electron spin coherence[1] and spin polarization[2] can be generated in chiral molecular systems. These effects emerge in systems where charge transport is dominated by incoherent hopping, mediated by spin-orbit and electronic exchange couplings. In this talk I will present the theory of these effects, and the general principles we can use to understand chirality induced spin effects in molecular systems. Furthermore, I will outline how chirality induced spin effects could be probed experimentally, and also demonstrate how this theory can explain the observed temperature dependent spin polarization in Photosystem I [3]. Chirality induced spin coherence and polarization effects should manifest in many chiral systems, and the ideas I will present have implications for the study of spin transport in systems relevant to chemistry, biology, and quantum technologies.



### References

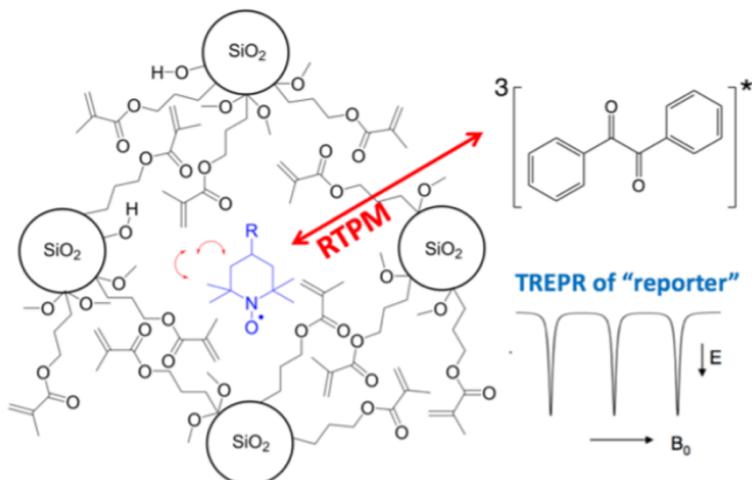
- [1] Fay, T. P. Chirality-Induced Spin Coherence in Electron Transfer Reactions. *J. Phys. Chem. Lett.* **12**, 1407–1412 (2021).
- [2] Fay, T. P. & Limmer, D. T. Origin of Chirality Induced Spin Selectivity in Photoinduced Electron Transfer. *Nano Lett.* **21**, 6696–6702 (2021).
- [3] Carmeli, I., Kumar, K. S., Heifler, O., Carmeli, C. & Naaman, R. Spin selectivity in electron transfer in photosystem i. *Angew. Chemie - Int. Ed.* **53**, 8953–8958 (2014).

# Structured (Non-Newtonian) Fluids Studied at the Molecular Level Using Steady-State and Time-Resolved EPR Methods

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Organic and inorganic photoexcited states often lead to free radicals that have strong chemically induced electron spin polarization (CIDEP), easily detected on the sub-microsecond time scale using time-resolved (CW) electron paramagnetic resonance spectroscopy (TREPR). Of the four known CIDEP mechanisms (radical pair mechanism (RPM), spin-correlated radical pair mechanism (SCRPM), triplet mechanism (TM), and radical-triplet pair mechanism (RTPM)), the latter is by far the least understood theoretically but may prove to be the most useful of all of them. Radical-triplet pairs involve electron spin state mixing and sometimes quenching of triplet states by stable doublet state free radicals such as nitroxides. This process can be extended to the study of stable nitroxide biradicals. The RTPM is attractive for investigation of excited state and radical dynamics for reasons: 1) the process is overall non-destructive, i.e., the triplet and the nitroxide eventually return to their electronic ground states with Boltzmann spin state populations, and 2) the resulting spectrum reports spin state information from the unobserved excited triplet state through the nitroxide, the intensity of which can be related to encounters between the two, driven by *translational* motion. Simultaneously, the recorded TREPR spectrum of the nitroxide contains line shape information related to *rotational* motion. The ability to observe and record both types of motion, especially in heterogeneous systems such as micelles, vesicles, bubbles, and emulsions is highly advantageous.



In this talk I will introduce the intricate features of the RTPM, with examples from my laboratory to show how structural, dynamic and mechanistic information can be obtained in a variety of chemical systems. These include micelles, vesicles, structured (non-Newtonian) fluids, polymers, and excited organic triplet states. I will use this talk as a platform to suggest new pathways that can exploit the RTPM for the investigation of more complex systems such as dye-sensitized solar cells, more complex structured fluids, and the dynamic properties of commercially important heteropolymers. The results represent one of the first reports of the physical properties on non-Newtonian fluids at the molecular level.

## Chemical Synthesis for the Creation of Atomically Precise Qubits

Danna Freedman

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The unique combination of atomic-scale tunability, reproducibility, and chemical specificity make paramagnetic molecules a paradigm-shifting category of materials. This capability has the potential to be transformative for developing a bespoke quantum ecosystem, as, for example, the requirements for a node within a quantum communications network are distinct and potentially orthogonal to those for a quantum sensor. Our team imbued molecular qubits with the same read-out approach as defect-based systems. To achieve this, we envisioned an inverse design problem whereby we mimicked the electronic structure with an orthogonal physical structure. Using transition metal chemistry, we designed the ground state, excited states and dynamics based on straightforward ligand field analysis. By coupling optical read-out with spatial precision, we seamlessly integrated a new class of materials with existing read-out technology.

Laorenza, D. W.; Kairalapova, A.; Bayliss, S. L.; Goldzak, T.; Green, S. M.; Weiss, L. R.; Deb, P.; Mintun, P. J.; Collins, K. A.; Awschalom, D. D.; Berkelbach, T. C.; Freedman, D. E. *J. Am. Chem. Soc.* **2021**, 143, 21350-21363.

## MolSpin – Introducing a versatile software package for spin chemistry

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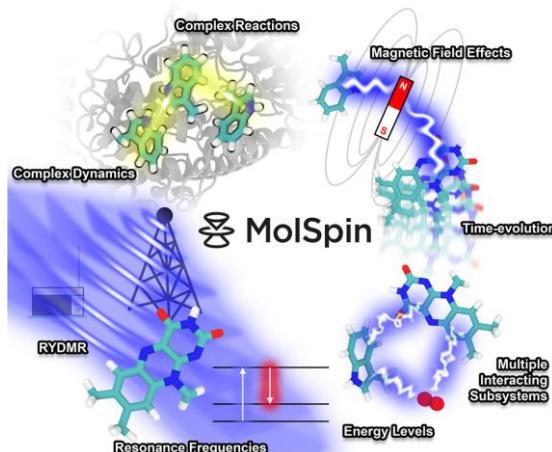
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Spin-dependent chemical reactions reveal fascinating mechanisms which are of high interest in the current scientific community. For instance, the application of an external magnetic field would affect the yield in simple radical reactions of formic acid formation [1]. Furthermore, spin-dependent reactions are believed to be the fundamental cause for endowing migratory birds with the ability to sense the Earth's magnetic field [2]. It is thus important to understand and describe the dynamics and interactions of spin systems of varied complexity. Not only the interactions between spins but also the influence of the environment exhibits an important aspect which leads to observable effects in experiments. The underlying theoretical framework to describe these effects relies on the Liouville-Von-Neumann equation. However, the solution of this equation is in most cases not only challenging for realistic systems but also requires the utilization of supercomputers.



**Figure 1** Examples of problems that can be described by MolSpin [3].

We have developed the software package MolSpin to efficiently solve and investigate spin dynamics for spin chemistry problems [3]. With MolSpin it is possible to describe spin-dependent reaction mechanisms, the influence of molecular motion and other perturbations using the Bloch-Redfield-Wangness formalism, and several other features. The software package is built to allow for an easy implementation of additional tasks and is thus suitable for challenging problems related to spin dynamics.

[1] T. C. Player, *J. Chem. Phys.*, **153**, 084303 (2020).

[2] J. Xu *et al.*, *Nature*, **594**, 535-540 (2021).

[3] C. Nielsen *et al.*, *J. Chem. Phys.*, **151**, 194105 (2019).

## High-multiplicity states in luminescent organic radicals

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Organic luminescent radicals present a new and exciting platform for exploring molecular functionalities at the interface of their unique optical and spin properties. [1] Near-unity internal quantum efficiency for red emission was demonstrated for donor-acceptor structures based on the tris(2,4,6-trichlorophenyl)methyl (TTM) radical. [2] This opens these materials towards applications in technologies ranging from organic light-emitting diodes and photovoltaics with eliminated triplet losses, to photomagnetic devices and molecular-scale information transfer.

Here we present a new family of molecules based on the TTM radical motif which contain high-multiplicity states in their emission mechanism. By combining light-induced EPR with ultrafast transient absorption and temperature-dependent transient luminescence spectroscopy we find a mechanism that uniquely supports both a high emission yield and a high yield of generation of the high-spin species. This is enabled by very low activation barriers between excited states, which arises from energy level matching in our molecular design. Pulsed EPR spectroscopy at both X and W-band frequencies allows us to characterize the potential of our system for future quantum information science applications.

### References

- [1] Teki, Y., *Chem. Eur. J.* **26**, 980 (2020).
- [2] Ai, X., Evans, E.W., Dong, S. *et al.*, *Nature* **563**, 536–540 (2018).



# Anisotropic magnetic-field effects in OLEDs at geomagnetic field strengths – a model for avian magnetoreception?

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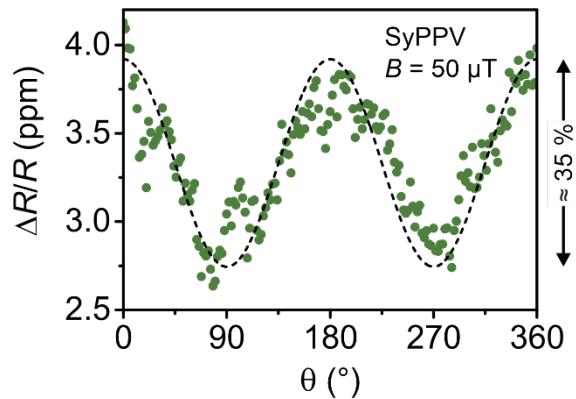
Although the effect of magnetic fields on the resistance and electroluminescence of organic light-emitting diodes (OLEDs) has been extensively studied, only little attention has been paid to the orientational dependence of these effects [1]. This aspect becomes of particular relevance when considering that the radical-pair mechanism, responsible for some of the magnetic-field effects in OLEDs, is currently the most promising candidate for the explanation of natural magnetoreception [2, 3].

We investigated magnetic-field effects in OLEDs in the regime of ultrasmall fields ( $< 2$  mT). For both device resistance and electroluminescence, an anisotropy is observed, with magnitude and symmetry depending on the magnetic-field strength. Our results show that OLEDs can act as a compass sensor at fields as weak as Earth's magnetic field. In order to gain a better understanding of the underlying mechanisms, we compare our experimental results to simulations based on the density-matrix formalism [4]. We identify microscopically anisotropic distributions of hyperfine fields in combination with finite macroscopic molecular order as the primary cause for the observed angle-dependent magnetic-field effects.

To disentangle the different sources of anisotropy in polymer OLEDs, electrically detected magnetic resonance (EDMR) can act as a useful tool since it reveals the hyperfine-field distributions experienced by charge-carrier spins. Angle-dependent EDMR measurements are considered, which enable constraints on the balance between microscopic and macroscopic sources of anisotropy to be formulated. Furthermore, our results indicate that the anisotropy in OLED magnetic-field effects decreases under resonant RF radiation, in analogy to the disorientation of birds exposed to RF magnetic fields [2].

## References

- [1] W. Wagemans *et al.*, *Phys. Rev. Lett.* **106**, 196802 (2011)
- [2] T. Ritz *et al.*, *Nature* **429**, 177 (2004)
- [3] J. Xu *et al.*, *Nature* **594**, 535 (2021)
- [4] S. Jamali *et al.*, *Nat. Commun.* **12**, 465 (2021)



Anisotropic relative magnetoresistance  $\Delta R/R$  of an OLED showing compass behavior at  $B = 50 \mu\text{T}$ .

## **Dynamic Nuclear Polarization using Sensitizer Radicals**

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Dynamic Nuclear Polarization (DNP) has already transformed the scope of NMR, permitting the study of molecular and materials surfaces, *in cell* NMR or highly dilute metabolites that would evade the detection of conventional NMR spectroscopy. Still, the vast majority of successful DNP experiments fall into a narrow range of sample conditions of dissolved or dispersed organic S=1/2 bi-radicals in a  $^1\text{H}$ -rich solvent glass. Even within this category, only a handful of biradical archetypes relying on bisnitroxides or nitroxide-trityl combinations yield reasonably high DNP performance, hence limiting the scope of DNP. Furthermore, the direct transfer of polarization from isolated electron spins to a surrounding nucleus is inefficient at high  $B_0$ . It is understood that utilizing coupled electron spins ( $e$ - $e$ ) can remedy this problem. Two distinct DNP mechanisms (Cross Effect (CE) and Thermal Mixing (TM)) rely on  $e$ - $e$  couplings (1's-100's MHz) to induce triple-flip transitions between two coupled  $e$  spins and a hyperfine coupled nucleus. The resonance condition is satisfied when the difference of the EPR frequencies of the coupled electron spins matches the nuclear Larmor frequency. These shortcomings ask for new strategies to design paramagnetic systems that span the optimal frequency and relaxation range for DNP. I will present two novel concepts that expand the scope of DNP: (1) The rational design of TM DNP that exploits a strongly coupled electron spin network, in which the difference of the EPR frequencies of the coupled electron spins matching the  $^1\text{H}$  Larmor frequency as generated from dipolar and exchange coupling between the coupled electron spins. High  $^1\text{H}$  TM DNP. A strongly coupled electron spin network is generated by exploiting spin clustering. (2) The concept of utilizing narrow line radicals to extract and sensitive DNP effects from higher than S=1/2 paramagnetic systems by frequency matching.

## Essential elements of photomagnetoreception in *Drosophila*

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Many animals can sense the Earth's magnetic field (MF) to aid with behaviours such as migration. It is proposed that MF can modulate the active concentration of the blue light photoreceptor, cryptochrome (CRY) [1]. In *Drosophila*, the active state of CRY correlates with the semiquinone radical of its flavin adenine dinucleotide (FAD) chromophore [2]. The canonical radical pair (RP) model of CRY-dependent magnetoreception involves magnetic effects on a spin correlated FAD / tryptophanyl RP following photoreduction of oxidised FAD following an electron transfer reaction within CRY [1]. Spectroscopic data from isolated animal CRY in solution suggest this RP is born in the singlet spin-state [3,4].

Despite numerous theoretical, spectroscopic and animal behaviour studies, several questions remain. What is the nature of the magnetically-sensitive RP *in vivo* and how is it made? How does a magnetic effect on a protein result in a behavioural response? What is the precise role of CRY? In contrast to migratory birds, the fruit fly, *Drosophila melanogaster*, represents a genetically-tractable *in vivo* model with which we can begin investigating such questions [5]. We have previously reported effects of MF on neuronal activity in *Drosophila* that are ostensibly CRY-dependent [6,7]. These studies suggest a critical role for the CRY C-terminal tail (CTT) in transducing the magnetic signal and the observed effects are most straightforwardly explained by a triplet-born RP. More recently, we have made the striking observation that the 52 C-terminal (CT) amino acids of CRY, which include the CTT but are missing the FAD binding domain, are sufficient to facilitate magnet responses at both the single neuron and organismal level [8]. These effects are enhanced by the addition of free FAD, but not riboflavin, which lacks the ability to autoreduce following intramolecular electron transfer.

I will discuss the implications of these findings on the possible nature of the RP, the signal transduction mechanism, and the likely role of CRY.

## References

- [1] P. J. Hore and H. Mouritsen, *Annu. Rev. Biophys.* **45**, 299 (2016)
- [2] A. T. Vaidya *et al.*, *Proc. Natl. Acad. Sci. USA* **110**, 20455 (2013).
- [3] Y.-T. Kao *et al.*, *J. Am. Chem. Soc.* **130**, 7695 (2008)
- [4] D. M. W. Sheppard *et al.*, *Sci. Rep.* **7**, 42228 (2017)
- [5] A. Bradlaugh *et al.*, *Quantum Rep.* **3**, 127 (2021)
- [6] R. Marley *et al.*, *Sci. Rep.* **4**, 5799 (2014)
- [7] C. N. G. Giachello *et al.*, *J. Neurosci* **36**, 10742 (2016)
- [8] A. Bradlaugh *et al.* *bioRxiv* doi: <https://doi.org/10.1101/2021.10.29.466426> (2021)

# The influence of the photoinduced reversible intramolecular processes on the electron spin polarization.

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The report will summarize the theoretical results and the experimental observations of the dynamic equilibrium studied with the framework of a two-site model. The light absorption in molecular conjugates often produce the metastable excited states that are in the dynamic equilibrium. This situation arises during energy transfer between several chromophores, in metal-centered porphyrins (dynamic Jan-Teller effect), in proton exchange reactions, etc. Hopping between different local environments causes changes in the spectral and kinetic properties of the spin system, which can be studied by the electron paramagnetic resonance spectroscopy. Reversible transitions contribute to a number of phenomena some aspect of which have been investigated recently [1-4]. They include the repopulation of the spin polarized states; the developing of the net polarization; modification of the spectral shape function; enhancement of the flip-flop transitions induced by the remote weakly-coupled spins.

We have developed a two-site model which allows the characterization the reversible exciton hopping in the molecular conjugates. The key point of the two-site model is the existence of the common state  $\rho = (k_B \rho_A + k_A \rho_B) / (k_A + k_B)$ , which diagonal matrix elements repopulate relatively slowly while the remaining states rapidly depopulate during the reversible transitions. The rate constants, repopulating the spin sublevels  $i$  and  $j$  of the common state, equal:

$$K_{ij} = \frac{8k_A k_B |(H_A - H_B)_{ij} / 2|^2}{(k_A + k_B)[(k_A + k_B)^2 + (H_A + H_B)_{ij}^2 / 4]}$$

Here,  $k_A$  and  $k_B$  are hopping rate constants,  $H_A$  and  $H_B$  are the spin-Hamiltonians of the sites A and B. These expressions provide simple relationship between the spectral and kinetic parameters of the excited molecules and allow analyzing the phenomena listed above.

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- [1] Y. E. Kand rashkin et al., J. Chem. Phys. 153, 094304 (2020)
- [2] M. G. D. Farra et al., Phys. Chem. Chem. Phys. 22, 19982–19991 (2020)
- [3] Y.E. Kand rashkin et al., J. Phys. Chem. Lett. 10, 4157–4163 (2019)
- [4] Y.E. Kand rashkin et al., J. Phys. Chem. C 124, 3939–3951 (2020)

## Weak-field magnetosensitivity cursed and blessed by the electron-electron dipolar coupling

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Magnetic field effects due to the Radical Pair Mechanism (RPM) are in principle well-understood and have been amply studied in chemical model systems. Yet, the question if radical pair processes could evoke significant magnetic field sensitivity in living systems in response to weak, geomagnetic-like magnetic fields is controversial. While in birds and a few other species, a compass sense has been attributed to a radical pair recombination reaction in the flavo-protein cryptochrome, it is unclear if the model can truly deliver the required sensitivity in a noisy biological environment.

The magnetosensitivity of radical pair reactions in weak magnetic fields is predominately inhibited by two factors: fast spin relaxation, in particular in radical pair systems involving reactive oxygen species (ROS), which are prevalent throughout biology; and the suppressive effect of inter-radical interactions, such as the unavoidable electron-electron dipolar (EED) interaction. In particular, the latter has mostly been neglected from theoretical treatments. This question has however gained new impetus as the previously assumed mutual compensation of EED and exchange interaction appears to not be able to mitigate this issue in cryptochromes.

Here, I will show how the ostensible issues and challenges of the RPM in the context of biological magnetic field effects can be overcome by:

- a) three-radical systems [1-2,5] for which the (primary) radical pair undergoes a spin selective scavenging reaction with a third, initially uncorrelated radical (a phenomenon dubbed the chemical Zeno effect),
- b) three-radical systems coupled via the electron-electron dipolar interaction as their predominant interaction mode [3-4], and thus undergoing spin dynamics not as a consequence of hyperfine interactions (such as for the RPM) but their mutual dipolar coupling,
- c) externally driven radical pair systems, for which the inter-radical distance is modulated to induce Landau-Zener-like non-adiabatic transitions in a magnetic-field sensitive manner, thereby overall supporting the notion that a live, i.e. externally driven magnetoreceptor, could be markedly more sensitive than its "dead", i.e. static, counterpart.

I will demonstrate how these effects can enable significant MFEs in weak magnetic fields in biological radical pairs, partly in the presence of swiftly relaxing radicals, such as ROS. For illustration, I will focus on the photo-reduction and reoxidation pathways in cryptochromes [5], with additional references to adult hippocampal neurogenesis and hippocampus-dependent cognition in mice, which are impaired in hypomagnetic fields [6], and lipid peroxidation.

- [1] D. R. Kattnig, P. J. Hore, *Sci. Rep.* **7**, 11640 (2017).
- [2] N. S. Babcock, D. R. Kattnig, *JACS Au* **1**, 2033 (2021).
- [3] R. H. Keens, S. Bedkihal, D. R. Kattnig, *Phys. Rev. Lett.* **121**, 096001 (2018).
- [4] N. S. Babcock, D. R. Kattnig, *J. Phys. Chem. Lett.* **11**, 2414-2421 (2020).
- [5] J. Deviers, F. Cailliez, A. de la Lande, D. R. Kattnig, *J. Chem. Phys.* **156**, 025101 (2021).
- [6] B. Zhang *et al.*, *Nature Comm.* **12**, 1174 (2021).

# Electronic Structure Contributions to Photoinduced Ground State Spin Polarization in Radical Elaborated Donor-Acceptor Molecules

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Radical-Elaborated Donor-Acceptor chromophores of the general form (diimine)Pt(dioxolene-radical) [1-6] that possess ligand-to-ligand charge transfer (LL'CT) excited states are excellent platforms for the generation and study of ground state electron spin polarization (ESP). The nature of the dioxolene → diimine LL'CT state is such that nearly a complete transfer of an electron is achieved, leading to  $(L^\cdot)Pt(L^+)-R^\cdot$  three spin excited state configurations where each spin is localized on a different component of the molecule (Donor, Acceptor, and Radical). A combination of magnetic susceptibility measurements on  $Tp^{Cum,Me}Zn(SQ-B-NN)$  (B = organic bridge, NN = nitronyl nitroxide) and related molecules, coupled with detailed magnetic circular dichroism studies of (bpy)Pt(CAT-B-NN) [7], have revealed the nature of the pairwise excited state exchange interactions that are critical to the control of electron spin polarization. The *Reversed Quartet Mechanism (RQM)* [8], which requires rapid mixing between excited trip-doublet and trip-quartet exchange coupled excited states, forms the basis for our understanding of photoinduced ESP in these radical elaborated chromophores. We have effectively expanded the *RQM* to include the presence of localized radical states (*e.g.*  ${}^2NN$ ,  ${}^4NN$ ) in order to explain the sign and the magnitude of the photoinduced ESP. These localized radical states can mix with the trip-doublet and trip-quartet exchange coupled excited states by an energy transfer mechanism, which is made efficient due to the close proximity of the donor, acceptor, and radical components of these molecules. Select examples of how this revised *RQM* explains the observed photogenerated ESP in these systems will be discussed.

## References

- [1] D. A. Shultz *et al.*, *J. Am. Chem. Soc.* **142**, 4916 (2020)
- [2] M. L. Kirk *et al.*, *Chem. Sci.* **11**, 11425 (2020)
- [3] M. L. Kirk *et al.*, *Chem. Sci.* **8**, 5408 (2017)
- [4] M. L. Kirk *et al.*, *J. Phys. Chem. Lett.* **13**, 872 (2022)
- [5] M. L. Kirk *et al.*, *Chem. Sci.* **12**, 13704 (2021)
- [6] M. L. Kirk *et al.*, *J. Am. Chem. Soc.* **143**, 10519 (2021)
- [7] B. W. Stein *et al.*, *J. Am. Chem. Soc.* **140**, 2221 (2018)
- [7] V. Rozenshtein *et al.*, *J. Phys. Chem. A* **109**, 5408 (2005)

# **Conformation Change of Exciton Pair: Spin-Entanglement Transport during Singlet Fission Studies by Time-Resolved EPR**

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Singlet fission (SF) is expected to exceed the Shockley–Queisser theoretical limit of efficiency of organic solar cells. Spin-entanglement in the triplet pair state via one singlet exciton is a promising phenomenon for several energy conversion applications including quantum information science. However, direct observation of the electron spin polarization by transports of entangled spin-states has not been demonstrated. Furthermore, vibronic mechanisms of the dissociation of the triplet excitons are poorly understood. In this study, time-resolved electron paramagnetic resonance has been utilized to observe the transports of the singlet and quintet characters generating spin-correlated correlated triplet pair (SCTP) by probing the electron spin polarization (ESP) generated in thin films of 6,13-bis(triisopropylsilylithynyl)pentacene.[1] We have clearly demonstrated that the ESP detected in resonance field positions of the individual triplet excitons are dependent on morphology and on detection delay time after laser flash to cause SF. The ESPs were clearly explained by quantum superposition[1,2,3] of singlet-triplet-quintet wavefunctions via picosecond triplet-exciton dissociation as the electron spin polarization transfer from strongly exchange-coupled singlet TT states to the weakly-coupled SCTP via spin-spin dipolar couplings with preserving conformations of the excitons. Although the coherent superposition of the spin eigenstates was not directly detected, the present interpretation of the spin correlation of the separated T+T exciton pair may pave new avenues not only for elucidating the vibronic role on the de-coupling[2,3,4] between the two excitons but also for scalable quantum information processing using quick T+T dissociation via one-photon excitation.

## **References**

1. Matsuda, S.; Oyama, S.; Kobori, Y. *Chem. Sci.* **2020**, *11*, 2934-2942.
2. Kobori, Y.; Fukui, M.; Nakamura, S.; Hasobe, T. *J. Phys. Chem. B* **2020**, *124*, 9411-9419.
3. Nakamura, S.; Sakai, H.; Nagashima, H.; Fukui, M.; Onishi, K.; Khan, R.; Kobori, Y.; Tkachenko, N. V.; Hasobe, T. *J. Phys. Chem. C* **2021**, *125*, 18287-18296.
4. Hasobe, T.; Nakamura, S.; Tkachenko, N. V.; Kobori, Y. *ACS Energy Letters* **2022**, *7* (1), 390-400.

# Paving the Way for Large-Scale Quantum Information Processing with more than 10 000 Multiqubit Entangled Nuclear Spin States in Hyperpolarized Molecular Solids

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Quantum entanglement has been realized on a variety of physical platforms including photons, quantum dots, trapped atomic ions, superconductors, and point defects in diamond and silicon carbide. Here we introduce specific molecular solids as promising alternative platforms. Our model system is triplet pentacene in a host single crystal at level anticrossing (LAC) conditions. First, a laser pulse generates the triplet state and initiates entanglement between an electron spin and 14 hyperfine coupled proton spins. This gives rise to large nuclear spin polarization. Subsequently, a resonant high-power microwave pulse disentangles the electron spin from the nuclear spins. Simultaneously, high-dimensional multiqubit entanglement is formed among the proton spins. We verified the initialization of  $2^{14}$  pure 14-qubit entangled nuclear spin states with an average degree of entanglement of  $0.77 \pm 0.03$  [1].

To address and coherently manipulate the multiqubit entangled states, efficient quantum gates are required. Recently, two related studies appeared that demonstrate the experimental implementation of scalable global or parallel quantum gates in chains of Coulomb-coupled trapped atomic ions [2,3]. In both gates, multiple parallel gate operations are achieved by applying phase- and/or amplitude-modulated laser pulses which introduce a qubit-state-dependent force on each qubit site. Similar gates can also be used in the dipolar coupled nuclear spin systems of the present study by applying properly modulated radio frequency pulses.

To assess the created quantum system, we determine the dimension of the entangled computational (Hilbert) space. Provided that solely inequivalent nuclei are employed, our experiment reaches a Hilbert space dimension of  $\text{dim} = 2^{14 \times 14} \approx 10^{59}$  which is many orders of magnitude larger than the dimension achieved in recent quantum advantage experiments using superconducting qubits [4] ( $\text{dim} \approx 10^{16}$ ) or photons [5] ( $\text{dim} \approx 10^{30}$ ). We therefore expect that the LAC experiment, introduced in this talk, paves the way for large-scale quantum information processing with more than 10 000 multiqubit entangled nuclear spin states. The total of these states depends on the number of  $I = \frac{1}{2}$  nuclei in an organic molecule which can be tailored by chemical synthesis.

- [1] G. Kothe *et al.*, *J. Phys. Chem. Lett.* **12**, 3647 (2021).
- [2] Y. Lu *et al.*, *Nature* **572**, 363 (2019).
- [3] C. Figgatt *et al.*, *Nature* **572**, 368 (2019).
- [4] F. Arute *et al.*, *Nature* **574**, 505 (2019).
- [5] H.-S. Zhong *et al.*, *Science* **370**, 1460 (2020).

## **Short-living charge-transfer state photovoltaic composite (poly-3-hexylthiophene/ semiconducting carbon nanotubes) detected by out-of-phase electron spin echo**

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Carbon nanotubes (CNT) are an interesting alternative to fullerenes or small molecules as electron acceptor material for active layer of organic solar cell. Promising results were obtained some time ago for bulk heterojunction blend of poly-3-hexylthiophene (P3HT) and semiconducting CNTs (s-CNT), with specially separated s-CNT from statistical mixture of metal CNT and s-CNT [1]. However, paramagnetic intermediates of photoelectric conversion (either free photogenerated charges or charge-transfer states) were not detected for such blends. Thus, the mechanism of photoelectric conversion in such polymer/ s-CNT systems is unclear, which complicates their further optimization.

Using out-of-phase electron spin echo technique with photoexcitation of P3HT/s-CNT blend by laser flash we detected the signal of the charge-transfer state. Two-pulse sequence  $\pi/4 - \tau - \pi - \tau - \text{echo}$  was used. Appearance of this signal is a solid proof that spin-correlated pair  $\text{P3HT}^+/\text{s-CNT}^-$  is formed upon photoexcitation. The out-of-phase ESEEM trace for this system is surprisingly close to that of P3HT/PC<sub>70</sub>BM [2], which implies similar distance of initial charge separation of 3 – 4 nm. However, out-of-phase electron spin echo signal decay with delay-after-flash (DAF) increase for P3HT/s-CNT blend is much faster, with characteristic time of 10  $\mu\text{s}$  at 30K. This point to higher geminate recombination rate for this system, which may be one of the reason of relatively poor photovoltaic performance of P3HT/s-CNT blend [1].

[1] S. Ren *et al.*, *Nano Lett.* **11**, 5316 (2011)

[2] E. A. Lukina *et al.*, *PCCP* **18**, 28585 (2016)

## **<sup>13</sup>C solid-state photo-CIDNP on a flavoprotein embedded in glassy sugar matrix**

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Phototropin is a blue light receptor containing flavin mononucleotide (FMN) in its LOV domain. After photoexcitation with blue light, the FMN forms a photoexcited triplet state which in natural occurring LOV domains reacts with a conserved nearby cysteine to form a covalent adduct. By mutation of the cysteine to a serine, the adduct formation is prohibited and the lifetime of the photoexcited <sup>3</sup>FMN is elongated. This induces a one-electron transfer from a tryptophan of the protein matrix (1 nm edge-to-edge distance) which in turn forms a radical pair as an intermediate leading to photochemically induced dynamic nuclear polarization (photo-CIDNP) signal enhancement in NMR which is observable in both solid and liquid states [1]. Here, isotope enrichment of <sup>13</sup>C and <sup>15</sup>N allows the selective detection of the hyperpolarized signals from both partners involved in the electron transfer.

The measurement time under illumination, however, is limited because of the generation of singlet oxygen by the photoexcited <sup>3</sup>FMN [2] which enhances the photodegradation of the protein. Besides, expensive and not straightforward isotope labelling can prohibit the search for photo-CIDNP in newly discovered proteins and impede further investigations on known ones. Therefore, an increase in stability of the protein under illumination can enable the use of two-dimensional solid-state photo-CIDNP NMR techniques for further investigations.

Here, we present an approach where the protein is embedded into a sugar glass matrix and measured with <sup>13</sup>C solid-state photo-CIDNP NMR. This has the advantage that the solid-state experiment can be performed at room temperature while simultaneously prolonging the measurement time to investigate unlabeled protein samples here presented for LOV1 of phototropin C57S.

### **References**

- [1] Y. Ding et al, Sci. Rep., **9**, 184436 (2019).
- [2] M. Petrencakova et al, Sci. Rep., **10**, 4119 (2020).

## Pumping and Pushing Around Electron Spins in Molecular Dyads and Triads

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Molecular dyads and triads are ideal model systems to study the spin evolution in spin correlated radical pairs and its dependence on an external magnetic field. For a series of model systems with a triarylamine electron donor and either naphthalene diimide or perylene diimide acceptor we demonstrate the magnetic field dependence of spin interconversion to be mainly caused by isotropic and anisotropic hyperfine coupling interaction over a magnetic field range up to 2 T.[1-3] Using a new, purely optical pump push spectroscopic method, we could prove the coherent nature of the S-T<sub>0</sub> spin evolution at a variety of fields. In fact, the dominant hyperfine coupling of the triarylamine nitrogen determines the observed quantum beating frequency.[4] For selected examples, also the g-value difference of the two radical centres gains importance at higher fields.

[1] J. H. Klein *et al.*, *J. Am. Chem. Soc.* **137**, 11011 (2015)

[2] J. Schäfer *et al.*, *Phys. Chem. Chem. Phys.* **20**, 27093 (2018)

[3] D. Mims *et al.*, *J. Chem. Phys.* **151**, 244308 (2019)

[4] D. Mims *et al.*, *Science* **374**, 1470 (2021)

## **Interaction of a photogenerated spin qubit pair with a stable radical in DNA hairpins**

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Tunable molecular systems that can generate entangled electrons, or spin qubit pairs (SQPs), are highly desirable for developments in quantum information science (QIS). Photogenerated SQPs can be initialized in a pure quantum state which exhibits relatively long coherence times, allowing for electron spin manipulation via optical and magnetic spectroscopy. DNA hairpins serve as a modifiable scaffold on which to study these multi-spin interactions, such as a SQP in conjunction with a stable radical. Such a multi-spin system is optimal for implementing spin manipulations that could be advantageous for executing quantum logic gates and spin teleportation. DNA hairpins also offer the possibility of individual qubit addressability and qubit scalability. Here, we examine a series of DNA hairpins that use naphthalenediimide (NDI) as the hairpin linker and chromophore, and guanine or an organic endcap as the terminal hole acceptor. A stable nitroxide radical is covalently attached to the hairpin to facilitate spin interactions between the SQP and stable radical. Electron paramagnetic resonance spectroscopy and ultrafast optical spectroscopy are utilized to explore the charge transfer rates and spin-spin interactions in these DNA hairpins to determine how the SQP pair interacts with the stable nitroxide radical, and how this modulates the overall dynamics of the system.

## **Magnetic field effect in bulk recombination of radicals**

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Magnetic field and spin effects in radical recombination reaction in a bulk of solvent are considered. The scale of the magnetic field effect and the influence of the hyperfine interactions as well as paramagnetic relaxation on its magnitude is estimated. The effect of ultrahigh magnetic field (UMF, tens of Tesla) on the recombination kinetics of short-lived radicals in the liquid phase is studied. The influence of the mechanism of equilibrium thermodynamic alignment of spins of the unpaired electrons of the radicals in UMF on the rate of spin-selective radical recombination is considered. The recombination rate constants are calculated by use of the theory of diffusion-controlled reactions in solution.

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## Newly developed techniques for measuring magnetic field effects

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Magnetic field effect (MFE) measurements on photochemical reactions on valuable biomolecules have faced difficulties, particularly low field effect (LFE) measurements are challenging because sample degradation reduces the quality of data[1]. We approached this problem with the following concepts in mind; (1) Time-resolved transient absorption (TA) measurements at smaller absorbance values reducing pump laser power; (2) Simultaneous broadband wavelength measurements; (3) Observing short (sub-microsecond) to long (millisecond) time scales with a single excitation pulse. In an attempt to fulfil these requirements, we propose the super-cavity ring-down spectroscopy (S-CRDS) method[2]. CRDS has already been demonstrated to be an effective method for TA measurements[3], but the problem is that only one absorption at a single delay time and wavelength can be measured with a single excitation pulse. Therefore, multiple excitations are necessary for acquiring the time profile in conventional CRDS. In this new method, a super-continuum light source with a broadband pulse train of a few MHz is used as a probe light. It is worth mentioning that this method uses a light source where the intensity of a single pulse increases sufficiently to produce a CRDS signal as the light source repetition frequency reduces.

Furthermore, an investigation into methodologies for finding spin coherence in low field effects is underway. In theory, the origin of the low field effect is thought to be a convolution of coherent spin motion and spin mixing via level crossing. Although we have previously used nanosecond field switching methodologies to determine radical pair lifetimes in the low field region[4], a detailed analysis of transient absorption changes associated with small field jumping in the low field regime is expected to provide new information on their spin dynamics.

Recently, AWG (arbitrary wave generator)-based pulse EPR and NMR have been developed for spin manipulation. We propose AWG-based chemical reaction control of radical pairs in both low and high magnetic field regimes. Here we present a theoretical calculation of an optimised RF field using local optimisation theory[5] and manifest AWG-based reaction control. In high field, the selection of the hyperfine lines and anisotropic control in the rotating frame can be achieved through the optimised RF (MW) field.[6].

### References

- [1] K. Maeda, A. J. Robinson et al. *Proc. Natl. Acad. Sci. USA.* 109, 4774-4779(2012).
- [2] K. Maeda, Japanese patent applied 特願 2022- 7803.
- [3] K. Maeda, S. R. T. Neil et al, *J. Am. Chem. Soc.* 133, 17807-17815(2011).
- [4] K. Maeda, Y. Naito, *Mol. Phys.* 117, 2709-2718(2019).
- [5] K. Masuzawa, M.Sato, M.Sugawara, K. Maeda, *J. Chem. Phys.* 152, 14301(2020)
- [6] A. Tateno et al. Poster presentation in SCM2022 would be expected.

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# Magnetic Control of Molecular Emission with Spin Qubit Pairs as the Basis of Quantum Sensing

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Photogenerated spin-correlated radical pairs (SCRPs) in electron donor–bridge–acceptor (D–B–A) molecules can act as molecular qubits and inherently spin qubit pairs. SCRP s can take singlet and triplet spin states, comprising the quantum superposition state. Coherence between two spin states and spin selective electron transfer reactions form the foundation of using SCRP s as qubits for sensing. We can exploit the unique sensitivity of the spin dynamics of SCRP s to external magnetic fields for quantum sensing applications including resolution-enhanced imaging, magnetometers, and magnetic switch [1]. Molecular quantum sensors, if realized, can provide new technological developments beyond what is possible with classical counterparts. We can use molecular emission, associated with spin-selective recombination of SCPRs, as a readout of spin state of SCRP s; optically “addressing” only one spin state of SCRP s.

Charge recombination to the electronic ground state typically occurs nonradiatively. We have demonstrated a rational design of donor-bridge-acceptor molecules that exhibit radiative charge recombination of radical pairs (charge-transfer emission) over long distances by taking advantage of intensity borrowing. Large excited-state electronic couplings and small energy gaps enable the observation of intramolecular long-range CT emission over unprecedented long distances. [2] Utilizing spin dynamics of radical pairs, we present a new strategy to control molecular emission by weak magnetic fields (< 1 Tesla), orders of magnitude smaller than the thermal energy at room temperature. We further demonstrated the tunability of the field response range by changing the energy levels of radical pairs; the field strength required to affect the emission, expressed in terms of exchange interactions,[3] experimentally validating, for spin-correlated radical pairs, the formalism developed by Anderson.[4] The implications of our study in quantum sensing applications will be discussed.

## References

- [1] T. Mani, *Chem. Phys. Rev.* **3**, 021301 (2022)
- [2] J.T. Buck, R.W. Wilson, T. Mani, *J. Phys. Chem. Lett.* **10**, 3080-3086 (2019)
- [3] J.T. Buck, T. Mani, *J. Am. Chem. Soc.* **142**, 20691-20700 (2020)
- [4] P.W. Anderson, *Phys. Rev.* **115**, 2–13 (1959)

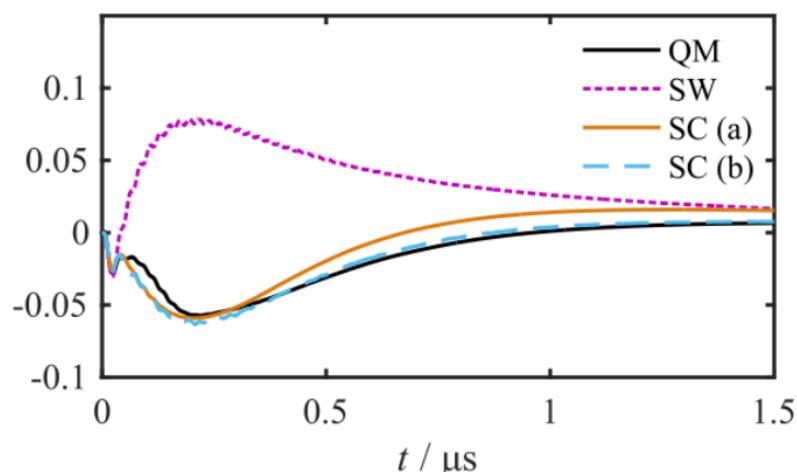
## Quantum and semiclassical methods for radical pair spin dynamics

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Peter Hore introduced us to the spin dynamics of radical pairs almost a decade ago. Since then, we have developed new semiclassical [1,2] and quantum mechanical [3-5] methods for simulating this spin dynamics, and applied them to a variety of interesting problems. For example we have recently calculated the exact quantum mechanical spin dynamics of a photo-excited carotenoid-porphyrin-fullerene (CPF) radical pair containing 45 hyperfine-coupled nuclear spins [6]. This was quite an achievement because the  $2^{47}$  coupled states in the Hilbert space would have made a standard quantum mechanical calculation quite impractical. We have also shown that an appropriate semiclassical approximation reproduces our quantum mechanical results for the CPF radical pair at a small fraction of the computational cost [6]. This talk will review these developments and use them to argue that the problem of simulating the spin dynamics of even rather complicated radical pairs has now been solved.



Magnetic field effect on the survival probability of a  $\text{C}^+\text{PF}^-$  radical pair from exact quantum mechanical (QM), Schulten-Wolynes (SW), and improved semiclassical (SC) calculations [6].

- [1] An improved semiclassical theory of radical pair recombination reactions. D. E. Manolopoulos and P. J. Hore, *J. Chem. Phys.* **139**, 124106 (2013).
- [2] Asymmetric recombination and electron spin relaxation in the semiclassical theory of radical pair reactions. A. M. Lewis, D. E. Manolopoulos and P. J. Hore, *J. Chem. Phys.* **141**, 044111 (2014).
- [3] An efficient quantum mechanical method for radical pair recombination reactions. A. M. Lewis, T. P. Fay and D. E. Manolopoulos, *J. Chem. Phys.* **145**, 244101 (2016).
- [4] A simple and accurate method for central spin problems. L. P. Lindoy and D. E. Manolopoulos, *Phys. Rev. Lett.* **120**, 220604 (2018).
- [5] Spin relaxation in radical pairs from the stochastic Schrodinger equation. T. P. Fay, L. P. Lindoy and D. E. Manolopoulos, *J. Chem. Phys.* **154**, 084121 (2021).
- [6] Quantum mechanical spin dynamics of a molecular magnetoreceptor. L. P. Lindoy, T. P. Fay and D. E. Manolopoulos, *J. Chem. Phys.* **152**, 164107 (2020).

## Recent progress in photo-CIDNP MAS NMR

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### (1) New review

Very recently, a new review about the history of the solid-state photo-CIDNP effect has been published. [1]

### (2) Theory & method development

Based on previous field-cycling MAS NMR data, magnetic field and orientation dependence were included into the theory. [2] “Spin-torch” experiments, transferring hyperpolarization into the cofactor pocket were reported. [3,4]

### (3) Analysis of photosynthetic reaction centers (RCs)

Structural studies on the donors of photosystem II [5], photosystem I [6] and purple bacterial reaction centers [7] demonstrated their differences.

### (4) Flavoproteins as agent for Photo-CIDNP MAS NMR

A LOV domain, i.e., a flavoprotein, shows a significant solid-state photo-CIDNP effect and allows for studying the mechanism by mutagenesis of the electron donating aromatic amino acid. [8-10]

## References

- [1] Jörg Matysik *et al.*, *Appl. Magn. Reson.* **53**, 521-537 (2022). DOI: 10.1007/s00723-021-01322-5.
- [2] Denis Sosnovsky *et al.*, *J. Chem. Phys.* **150**, 094105 (2019). DOI: 10.1063/1.5077078.
- [3] Pavlo Bielytskyi, *et al.*, *Appl. Magn. Res.* **50**, 695-708 (2019). DOI: 10.1007/s00723-019-1110-x.
- [4] Pavlo Bielytskyi *et al.*, *J. Magn. Reson.* **298**, 64-76 (2019). DOI: 10.1016/j.jmr.2018.11.013.
- [5] Denis G. Artukhin *et al.*, *J. Phys. Chem. B* **25**, 3066-3079 (2021). DOI: 10.1021/acs.jpcb.0c10656.
- [6] Geertje J. Janssen *et al.*, *Magn. Reson.* **1**, 261-274 (2020). DOI: 10.5194/mr-1-261-2020
- [7] Daniel Gräsing *et al.*, *Sci. Rep.* **9**, 10528 (2019). DOI: 10.1038/s41598-019-46903-4.
- [8] Yonghong Ding *et al.*, *PhysChemChemPhys* **23**, 16767 (2021). DOI: 10.1039/d1cp02217b.
- [9] Yonghong Ding *et al.*, *Sci. Rep.* **10**, 18658 (2020). DOI: 10.1038/s41598-020-75627-z.
- [10] Yonghong Ding *et al.*, *Sci. Rep.* **9**, 18436 (2019). DOI: 10.1038/s41598-019-54671-4.

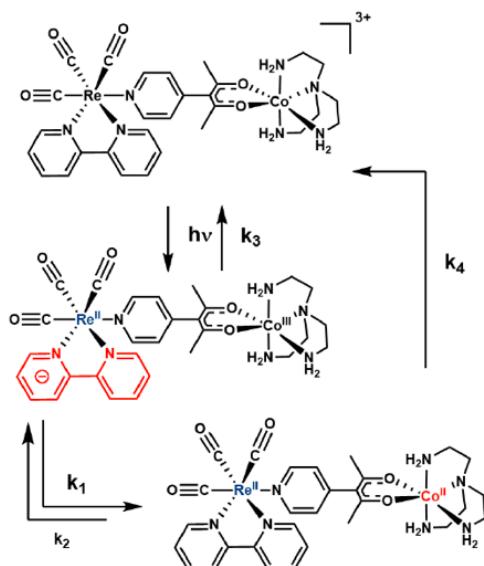
## Spin-based Control of Excited-state Reactivity

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Electron spin is a fundamental property of Nature. Although many of the more common physical observables linked to spin are well documented, the degree to which spin helps to define the chemistry of molecular systems is not as clear. This question constitutes the conceptual underpinning of our research effort. Specifically, we are interested in the design of donor-acceptor molecular assemblies that will allow us to probe the extent to which spin and spin-polarization manifests in their physical and photophysical properties. Previous work from our lab demonstrated that the concept of conservation of angular momentum is a necessary consideration for dipolar energy transfer [1]. We have now extended this concept to demonstrate that one can leverage this idea to differentiate between competing energy and electron transfer reaction pathways following photoexcitation of a donor-acceptor assembly [2]. This presentation will describe the synthesis and characterization of new compositional platform that we have developed based on a dimensional reduction of our previously published work that allows for the creation of systems amenable to both electron and energy transfer from an initially formed MLCT excited state (Figure 1). Time-resolved emission and absorption data will be described that reveal selectivity for excited-state electron transfer to Co(III) despite favorable conditions for dipolar energy transfer due to the introduction of a spin restriction for energy transfer. The possibility of generalizing this approach to more complex systems will also be discussed.



**Figure 1.** Proposed mechanism of photo-induced electron transfer in a spin-tailored donor-acceptor system.

[1]. D. Guo *et al.* *Science* **334**, 1684-1687 (2011)

[2]. M.D.Woodhouse *et al.*, manuscript in preparation.

## **Carrier and Spin Dynamics in Organic Photovoltaic Thin Films Studied by Simultaneous Optical and Electrical Detection**

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Photovoltaics based on organic materials has been a center of focus in research in material developments toward decarbonization and sustainable society. For improvement of the energy conversion efficiency, it is of much importance to quantify how many charged carriers are generated by the incident photon, how fast they move in response to an electric field, and how efficiently they are collected by the electrodes. In amorphous/semitransparent organic films, however, this is actually a difficult task because the photocarriers transport among inhomogeneous local sites, which gives rise to a broad distribution of the energy and mobility. Conventional electrical measurement of carrier dynamics has a critical problem that an effect of highly mobile carriers is overestimated since the photocurrent is linear to the product of the mobility and concentration of carriers. This is one reason for large variations in measured quantities (such as mobility) for an identical material among devices and methods.

We have been tackling this problem by simultaneous optical and electrical detection (SOED) for an identical thin film device.<sup>[1]</sup> Transient optical absorption is detected simultaneously with transient photocurrent, former of which quantitatively tracks decay of the total carrier concentration by recombination / electrode collection. This technique enables us to differentiate whether the photocurrent decay is due to extinction of charged species itself or change in the mobility distribution towards lower side, latter of which is mainly due to so-called trapping. Furthermore, magnetic field effect (MFE) on SOED signals allows us to selectively observe the spin selective dynamics of paramagnetic pair species such as electron-hole pairs.

In the talk, our recent results listed below will be discussed.

- 1) Non-geminate electron-hole pair dynamics in a bulk heterojunction (BHJ) thin film.
- 2) Electrode collection dynamics in a real BHJ solar cell device.
- 3) Spin selective geminate recombination in a dye-doped poly(*N*-vinylcarbazole) film.

These results demonstrate significance of trapping for carrier and spin dynamics in organic film materials.

### **References**

- [1] T. Miura, R. Akiyama, S. Kobayashi, T. Ikoma, *J. Phys. Chem. C* **125**, 22668 (2021).

# **The role of the electron's spin in closed shell chiral systems**

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## **Abstract**

Spin based properties, applications, and devices are commonly related to paramagnetic or magnetic molecules and materials. However, in the case of chiral molecules or materials, any electric field breaks the entanglement of the electrons in the singlet state. This effect results in interesting properties related to the interaction among chiral objects and between them and magnetic elements. The new effects will be described and their manifestation in spin selective chemistry and enantiospecific interactions will be described.

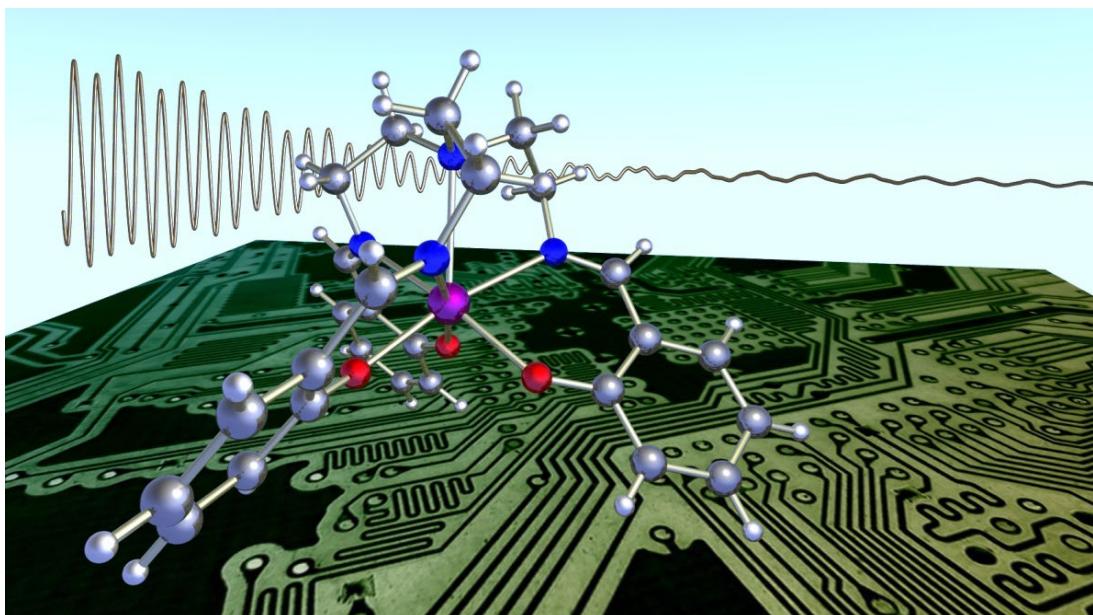
The phenomenon is related to the Chiral Induced Spin Selectivity (CISS) effect and it was found, among others, in bio-molecules and in bio-systems as well as in chiral oxides and in chiral perovskites. It has interesting implications for the production of new types of spintronics devices, in controlling magnetization, and on electron transfer and conduction. It also enables the introduction of new type of catalysts, especially for oxygen related processes.

## Molecular Lanthanide Complexes for Quantum Technologies

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**Figure 1** Illustration depicting the quantum coherence properties of Yb(trensal) and its suitability for surface deposition in view of its potential use in Quantum Technologies.

We have shown, in collaboration with many co-workers, that molecular Lanthanide-based coordination complexes hold potential for use as physical supports for the implementation of quantum bits and quantum gates in Quantum Information Technology devices. We studied the coherent dynamics of electronic and nuclear spins in Yb(trensal), by pulsed magnetic resonance experiments on oriented single-crystals.<sup>1,2</sup> The coupled electronic qubit-nuclear qudit nature of this system allowed to propose a scheme for intrinsic implementation of efficient quantum error correction schemes.<sup>2</sup> In further work, we investigate the multifrequency single crystal c.w.- and pulse EPR spectra of Gd(trensal), to characterize the energy spectrum and coherent magnetisation dynamics of its  $^8S_{7/2}$  ground term.

[1] K. S. Pedersen *et al.*, *J. Am. Chem. Soc.*, **138**, 5801 (2016).

[2] R. Hussain *et al.*, *J. Am. Chem. Soc.*, **140**, 9814 (2018).

# Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis: A Time-Resolved 130 GHz EPR and ENDOR Study

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Photosynthetic reaction centers, RCs, are integral membrane proteins which capture and convert sunlight into chemical energy via efficient charge separation achieved following photoinitiated sequential electron transfer (ET) steps. The fast primary electron transfer steps create a so-called spin-correlated radical pair, SCRP, which also referred as an entangled two electron spins qubit pair. This entangled state contains detailed information about weak magnetic interactions, structure, and dynamics of local protein environments involved in the charge separation events. However, extracting this information is still a great challenge. The high spectral resolution of 130 GHz time-resolved EPR and ENDOR, combined with extra resolution afforded by deuterated proteins, allows us to provide new mechanistic insight into the regulation of light-induced electron transfer in type I and type II RCs. Type II RCs like the bacterial RC (bRC) or Photosystem II (PSII) have two asymmetric branches of ET cofactors which fulfill different functions, while in type I RCs such as Photosystem I (PSI) both branches fulfill the same function.

In PSI, the EPR spectra of SCRPs formed in each of the two quasi-symmetric branches of ET cofactors, A or B, exhibit distinctive line shapes.<sup>1,2</sup> Biochemically modified PSI samples were used to analyze the asymmetry of electron transfer as a function of temperature, freezing condition, and temperature cycling.<sup>3</sup> Analysis on the temperature dependency support a dynamic model in which the conformational states of the protein regulate the directionality of electron transfer.

In the bRC, electron transfer is unidirectional proceeding down one branch of cofactors. Using time-resolved ENDOR we were able to probe protons located along the electron transfer pathway between the donor-acceptor SCRP. Spectroscopic analysis reveals hydrogen-bonding interactions involved in regulating the route electrons travel from the primary donor through the RC protein during charge separation.<sup>4,5</sup> This work adds to our understanding of Nature's control of primary electron transfer reaction mechanisms; fundamental insight that provides a basis for developing advanced solar energy conversion systems based on photosynthetic designs.

## References

1. O.G. Poluektov *et al.*, *J. Am. Chem. Soc.* **127**, 11910 (2005).
2. O.G. Poluektov *et al.*, *J. Phys. Chem. B*, **119**, 13771 (2015).
3. O.G. Poluektov *et al.*, *J. Phys. Chem. B*, **123**, 7536 (2019).
4. O.G. Poluektov *et al.*, *J. Am. Chem. Soc.* **126**, 1644 (2004).
5. O.G. Poluektov *et al.*, *J. Phys. Chem. B*, **125**, 4025 (2021).

## Tuning the optical and magnetic properties of photogenerated three-spin systems

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Photogenerated organic triplet-doublet systems hold great promise for a range of technological applications in the emerging field of molecular spintronics, including the areas of quantum information technology and artificial photosynthesis.<sup>[1–4]</sup> These systems are typically composed of a chromophore that is covalently linked to a stable radical. The proximity of the radical alters the excited state dynamics of the chromophore and, frequently, the radical acts as an efficient triplet sensitizer by enhancing the intersystem crossing rate. The further development of any applications involving such systems will crucially depend on our ability to control the magnetic properties of these materials, which requires a profound understanding of the underlying competing excited state deactivation processes.

In this contribution, we present our recent results obtained for a range of chromophore–radical compounds comprising systematic modifications of the molecular structure. Perylene diimide (PDI) is used as the chromophore in all cases, but the compounds differ with respect to the number of PDI core substituents, linker type, linker length, and type of the radical. We show that the combination of several complementary spectroscopic techniques, including femtosecond transient UV-vis absorption and transient pulse EPR spectroscopies, allows us to establish a complete picture of the excited state deactivation processes and interactions between the two spin centers. Combining the results from several studies on related structures with insight from ab-initio calculations, we shed light on the factors influencing the rate and yield of triplet formation as well as the magnitude of the exchange interaction between chromophore triplet and radical.

## References

- [1] Y. Teki, *Chem. Eur. J.* **26**, 980 (2020)
- [2] M. R. Wasielewski *et al.*, *Nat. Rev. Chem.* **4**, 490 (2020)
- [3] O. Nolden *et al.*, *Chem. Eur. J.* **27**, 2683 (2021)
- [4] M. Mayländer *et al.*, *J. Am. Chem. Soc.* **143**, 7050 (2021)

## **Photo-CIDNP for High Throughput Drug Screening**

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Photo-chemically induced dynamic nuclear polarization (photo-CIDNP) is a promising solution to the inherent lack of sensitivity in NMR spectroscopy. It is particularly interesting in biological systems since it operates in water, at room temperature, and it can be repeated if the bleaching of the system can be controlled. However, the photo-CIDNP signal enhancement is well below those of other hyperpolarization techniques. While DNP, PHIP, and SABRE reach polarization enhancements of  $10^3$  to  $10^4$ -fold, photo-CIDNP enhancement is typically only one order of magnitude for  $^1\text{H}$  and two orders of magnitude for  $^{13}\text{C}$  in the amino-acids tryptophan and tyrosine. We recently reported on a novel dye ligand pair with Atto Thio 12 and HOPI, which is a photo-oxidation product of tryptophane, getting a  $^1\text{H}$  signal enhancement of 120-fold at 600 MHz, 380-fold enhancement at 200 MHz and over 1200 fold enhancement on  $^{13}\text{C}$  [1,2]. In addition, we started to build up a small molecule chemical library of ca 200 photo-CIDNP active compounds [3] and demonstrated, that photo-CIDNP enhancement is inversely related to ligand protein binding establishing a novel approach to screen for lead compounds in drug research. Using a flow cell-based approach 1000 compounds per day can be screened for qualitative and eventually quantitative ligand affinity studies of small molecules binding to any protein target of interest.

### **References should be listed as below**

- [1] Torres *et al.*, *Phys Chem Chem Phys.* **23**, 6641 (2021)
- [2] Sobol *et al.*, *J. Chem. Phys.* **151**, 234201 (2019)
- [3] Torres *et al.*, *Magn. Reson.* **2**, 321 (2021)

K.M. Salikhov

Comment on the spin-selective recombination term in the kinetic equation for the radical pair density matrix

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Annotation.

In the scientific literature, there are several proposals for taking into account the spin-dependent recombination of radical pairs in the equation of motion for their density matrix.

In my report, I plan to bring these proposals and express my point of view.

References

1. M. Tomkiewicz, A. Groen, M. Cocivera, J. Chem. Phys. **56**, 5850 (1972)
2. J. B. Pedersen, J.H. Freed, J. Chem. Phys. **58**, 2746 (1973); **59**, 2869 (1973)
3. R. Haberkorn, Mol. Phys. **32**, 1491 (1976)
4. U.E. Steiner, T. Ulrich, Chem. Rev. **89**, 51 (1989)
5. A.I. Shushin, Chem. Phys. **144**, 201 (1990)
6. J.A. Jones, P.J. Hore, Chem. Phys. Lett. **488**, 90 (2010)
7. K.M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, A. L. Buchachenko. Spin Polarization and Magnetic Effects in Radical Reactions. Academic Kiado Budapest, Elsevier Amsterdam, p.419, (1984).

# **Exploring Photogenerated Radicals in Self-assembled Urea-Tethered Triphenylamines**

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Triphenylamine (TPA) radical cations stabilized by substitution on the *para*-position hold promise as spin-containing building blocks for polymer magnets. Self-assembly potentially affords an alternative strategy for stabilizing organic radicals, which might relax constraints on TPA substituents. Herein, we examine the effect of assembly on the stability of photogenerated radicals of urea tethered triphenylamines. Triphenylamine containing *bis*-urea macrocycles and urea tethered linear analogues were synthesized and their crystal structures determined.[1-3] These crystalline materials control the distinct microenvironments around the photoactive groups. Upon excitation in solution, triphenylamines with unsubstituted *para*-positions form radical cations that rapidly degrade. Upon UV-irradiation of the supramolecular assemblies, both linear and macrocyclic systems display remarkably persistent and regenerable radicals as monitored by EPR. The line shape of the EPR spectra and quantity of radicals can be modulated by polarity and by presence of heavy atoms, either covalently connected and or within supramolecular complexes. Transient absorption spectroscopy, cyclic voltammetry and time-dependent density function theory were also used to probe formation of these radicals and follow photoinduced electron transfer from host to guest.[4]

## **References:**

- [1] Sindt, A. J.; DeHaven, B. A.; McEachern, D. F.; Dissanayake, M. M.; Smith, M. D.; Vannucci, A. K.; Shimizu, L. S. *Chem. Sci.* **2019**, *10*, 2670-2677.
- [2] Sindt, A. J.; DeHaven, B. A.; Goodlett, D. J.; Hartel, J. O.; Ayare, P. J.; Du, Y.; Smith, M. D.; Brugh, A. M.; Forbes, M. D. E.; Bowers, C. R.; Vannucci, A. K.; Shimizu, L. S. *J. Am. Chem. Soc.* **2020**, *142*, 502-511.
- [3] Hossain, M. S.; Sindt, A. J.; Goodlett, D. W.; Shields, D.; O'Connor, C. J.; Antevska, A.; Krakalos, S. G.; Smith, M. D.; Garashchuk, S.; Do, T. D.; Gudmundottir, A.; Shimizu, L. S. *J. Phys. Chem. C* **2021**, *125*, 19991-20002.
- [4] Islam, Md. Faizul; Sindt, Ammon J.; Hossain, Muhammad Saddam; Ayare, Pooja, J.; Smith, Mark D.; Vannucci, Aaron K.; Garashchuk, Sophya; Shimizu, Linda S. *Phys. Chem. Chem. Phys.*, **2021** *23*, 23952-23960.

## Magnetic Exchange Interactions in Both Ground- and Excited States: Evaluation of Electronic Coupling Parameters and Photoinduced Electron Spin Polarization

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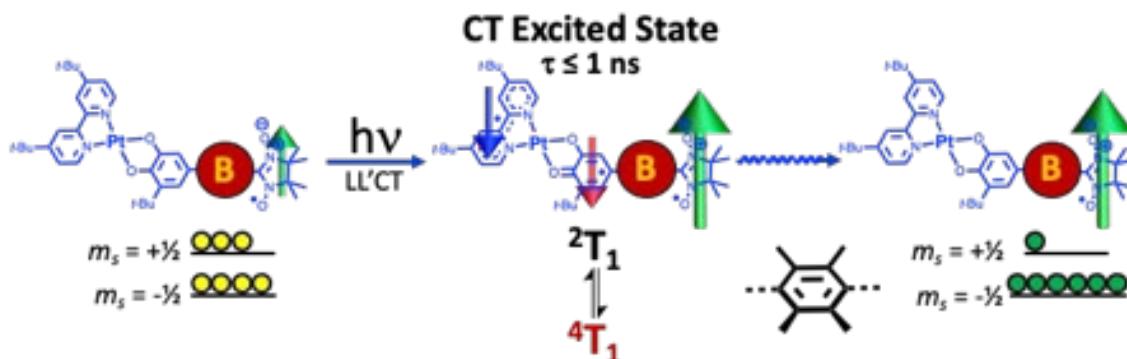
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Magnetic exchange interactions ( $J$ ) between unpaired spins play a crucial role in molecule-based magnetic-, electronic-, and spintronic materials, as well as photophysics, and quantum information science. This presentation will describe our research efforts focused on understanding exchange coupling in donor-acceptor biradical ligand complexes, and how this leads to control of ground-state electron spin polarization in radical-substituted donor-acceptor complexes of (primarily) platinum(II).

Metal complexes of donor-acceptor biradical ligands comprised of  $S = \frac{1}{2}$  semiquinonate (SQ, donor) and  $S = \frac{1}{2}$  nitronylnitroxide (NN, acceptor), offer a unique molecular platform to evaluate bridge-dependent electronic- and magnetic exchange coupling ( $H$  and  $J$ , respectively) in the context of a valence bond-type configuration interaction model.<sup>1-3</sup> These molecules serve as ground-state analogs of charge-transfer (CT) excited states, affording us the ability to predict the relative energies of multi-spin CT excited states. In solvent glasses, equilibria between an excited doublet ( $^2T_1$ ) and closely-spaced quartet states (e.g.,  $^4T_1$ ) provides a pathway for non-Boltzmann populations of the  $^2T_1$  state via the reversed quartet mechanism.<sup>4</sup> Rapid nonradiative decay of the  $^2T_1$  state transmits this spin polarization to the ground state where it is detected as a time-resolved EPR signal. Our results show that the magnitude and sign of the spin-polarized EPR signal is correlated with the exchange parameter between SQ and NN ( $J_{SQ-NN}$ ) in the CT excited state.<sup>5-7</sup> Moreover,  $J_{SQ-NN}$  can be tuned through rational synthetic design.



### References

- [1] D. A. Shultz *et al.*, *J. Am. Chem. Soc.* **142**, 4916 (2020)
- [2] M. L. Kirk *et al.*, *Chem. Sci.* **11**, 11425 (2020)
- [3] M. L. Kirk *et al.*, *Chem. Sci.* **8**, 5408 (2017)
- [4] V. Rozenstein *et al.*, *J. Phys. Chem. A* **109**, 5408 (2005)
- [5] M. L. Kirk *et al.*, *J. Phys. Chem. Lett.* **13**, 872 (2022)
- [6] M. L. Kirk *et al.*, *Chem. Sci.* **12**, 13704 (2021)
- [7] M. L. Kirk *et al.*, *J. Am. Chem. Soc.* **143**, 10519 (2021)

## Understanding electron spin decoherence

Organic radicals and paramagnetic transition metal complexes can serve as molecular electron spin qubits for potential applications in quantum information science and technology. An important prerequisite for these applications is a long coherence lifetime. We present an experimental and theoretical investigation into the decoherence mechanism of nitroxide and other organic radicals, who possess decoherence times (phase memory times) on the order of 5  $\mu$ s below 50 K in frozen protonated aqueous solutions, and more than an order of magnitude longer in fully deuterated environments. The experiments reveal that the decoherence time depends critically on the bulk proton concentration and on local spatial correlations between protons. Fully coherent many-body quantum dynamics simulations of the electron spin and about 1000 neighbouring hydrogen nuclei (protons and deuterons) quantitatively reproduce the measured coherence decays. This demonstrates that the electron spin decoherence is driven by many small clusters of magnetic nuclei, in particular geminal proton pairs ( $\text{CH}_2$  or  $\text{OH}_2$ ), that interact among themselves and with the electron spin.

# Charge-separated states in fullerene- and non-fullerene-based organic photovoltaics probed by EPR

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Organic photovoltaics hold promise as a flexible, cost-efficient, and sustainable solution to the challenges posed by an ever-growing energy demand. Organic solar cells are based on an active layer consisting of a blend of electron donating and accepting organic semiconductors. Photoexcitation generates strongly bound excitons that diffuse to the donor-acceptor interface to form an interfacial charge-transfer state, followed by separation into positive and negative charge carriers, which can then be extracted to generate electricity.

In recent years, the development of new electron acceptor molecules, to replace the fullerene-based ones traditionally used, has led to significant increases in power conversion efficiencies, which are now close to reaching the 20% threshold.<sup>1</sup> Despite this remarkable progress, a detailed mechanistic understanding of the energy conversion process is still missing, with the charge separation step at the donor-acceptor interface being the least well understood aspect of organic photovoltaics. Recent evidence based mainly on optical spectroscopies points towards significant differences in this crucial step between solar cells based on fullerene acceptors and on novel fused-ring electron acceptors.<sup>2</sup>

We are using EPR spectroscopy to investigate the nature and dynamics of paramagnetic species generated upon photoexcitation in blends of fullerene acceptors ( $\text{PC}_{61}\text{BM}$ ) or fused-ring electron acceptors (ITIC, Y6) with matching donor polymers (PBDB-T, PBDB-T-2F). At short times after laser excitation, the transient EPR spectra show the clear signatures of spin-correlated pairs of charges on donor and acceptor molecules, followed by evolution of the initially spin-polarised signal to fully absorptive spectra of the donor and acceptor radicals at long times. Analysis of the time- and temperature-dependence of this evolution reveals distinctly different behaviours for different donor:acceptor blends, hinting at differences in the charge separation process.

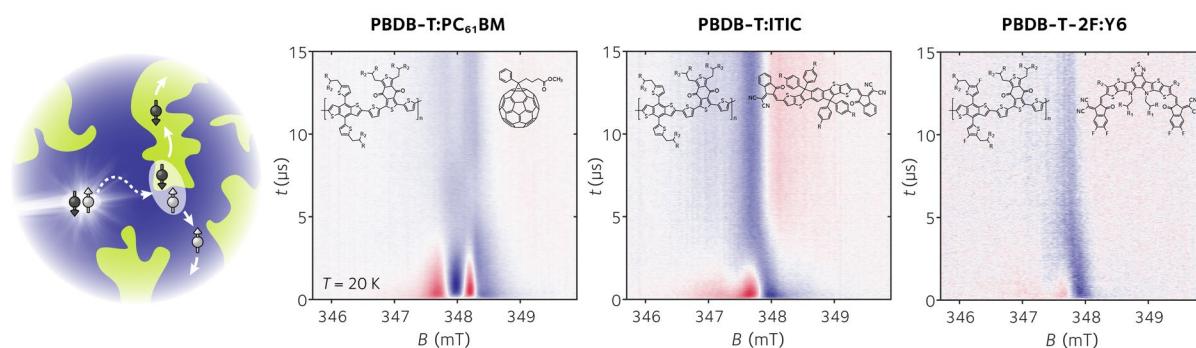


Figure 1. X-band transient EPR spectra recorded on blends of PBDB-T:PC<sub>61</sub>BM, PBDB-T:ITIC and PBDB-T-2F:Y6 at 20 K after photoexcitation at 532 nm.

- [1] M. Moser, A. Wadsworth, N. Gasparini, I. McCulloch, *Adv. Energy Mater.* **11**, 2100056 (2021).
- [2] A. Armin, A., W. Li, O.J. Sandberg, Z. Xiao, L. Ding, J. Nelson, D. Neher, K. Vandewal, et al. *Adv. Energy Mater.* **11**, 20003570 (2021).

# $\pi$ -Topology, Ultrafast Excited-State Dynamics, and FET Performance of Remarkably Photochemically Stabilized Pentacene Derivatives with Radical Substituents

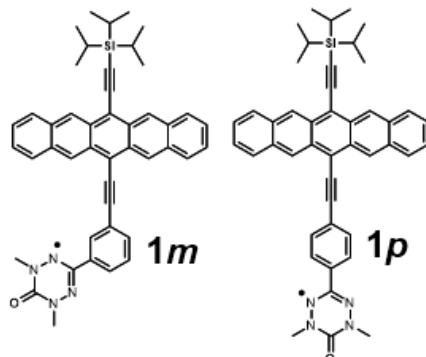
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In our previous works, we reported a novel strategy for the photochemical stabilization (radical photostabilization) that utilized the unique excited-state spin dynamics induced by the attachment of the  $\pi$ -radical substituent(s) to the pentacene (Pn) moiety [1-3]. Thus, Pn derivatives with one or two  $\pi$ -radical substituent(s) were significantly more stable against photodegradation because of the enhanced/accelerated intersystem crossing (EISC) of the Pn moiety. In the present work [4], we report novel pentacene-radical-linked systems (**1m** and **1p**) with the topologically different  $\pi$ -orbital networks ( $\pi$ -topology). They showed a remarkable improvement in photochemical stability, which was 187 (139) times higher than that of 6,13-bis(triisopropylsilyl)pentacene (TIPS-Pn). Transient absorption (TrA) spectroscopy showed that this remarkable photostabilization is due to the ultrafast intersystem crossing induced by effective  $\pi$ -conjugation between the radical substituent and pentacene moiety owing to their molecular planarity. It is also worthy of notice that the intersystem crossing of the purely organic compounds without heavy atoms is realized in the sub-femtosecond region. The relationship between  $\pi$ -topology and the photochemical stability is also discussed based on the excited-state dynamics. In addition,  $\pi$ -topological control of the excited-state dynamics was realized and applied to the enhancement of photochemical stability. Field-effect-transistor (FET) performance was also evaluated using **1m** and **1p** as the hole transport materials.



- [1] Y. Kawanaka, A. Shimizu, T. Shinada, R. Tanaka, Y. Teki, *Angew. Chem. Int. Ed.* **52**, 6643 (2013). [2] A. Ito, A. Shimizu, N. Kishida, Y. Kawanaka, D. Kosumi, H. Hashimoto, Y. Teki, *Angew. Chem. Int. Ed.* **53**, 6715 (2014). [3] A. Shimizu, A. Ito, Y. Teki, *Chem. Commun.* **52**, 2889 (2016). [4] N. Minami, H. Hashimoto, Y. Teki et al., *Phys. Chem. Chem. Phys.* accepted [DOI: 10.1039/d2cp00683a] [back cover].

## The Role of the Radical Pair Mechanism in Avian Magnetoreception

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Although it has been known for half a century that night-migratory songbirds can detect the strength and direction of the Earth's magnetic field for the purposes of orientation and navigation, the primary sensory mechanisms responsible for this fascinating feat are still obscure. Schulten's suggestion in 1978 [1] that this capability might be driven by a quantum mechanical process involving a pair of photoinduced radicals was long considered to be an exotic and highly unlikely hypothesis. However, with the discovery of cryptochromes [2], a family of blue light photoreceptor proteins, this radical pair hypothesis has taken centre stage in the discussion of animal magnetosensitivity and is now, arguably, the most likely mechanism to drive this fascinating process.

Here we report that the photochemistry of cryptochrome 4 from the night-migratory European robin (*Erythacus rubecula*, ErCry4) is indeed magnetically sensitive *in vitro*, and compare the results to those found for Cry4 from two non-migratory bird species, chicken and pigeon. Site-specific mutations of ErCry4 in combination with Electron Paramagnetic Resonance studies are used to demonstrate the roles of four successive flavin-tryptophan radical pairs in generating magnetic field effects and in stabilising potential signalling states [3].

[1] Schulten, K.; Swenberg, C. & Weller, A. *Z. Phys. Chem.*, **111**, 1–5 (1978)

[2] Ahmad, M. & Cashmore, A.R., *Nature*, **366**, 162–166 (1993)

[3] Xu J. *et al.*, *Nature*, **594**, 535-540 (2021)



## Optically Detected Magnetic Resonance Studies of the Chl F Synthase Enzyme

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Photosynthetic organisms live in a wide variety of environments with very different and variable light conditions. In particular, plants living in the understory can receive relatively little light in the middle of the visible spectrum at times because it is absorbed by the plants above them. It was recently discovered that some oxygenic organisms have a complex set of genes that allow them to adapt to differing light conditions. These genes and the regulatory process associated with them is known as far red light photoacclimation (FaRLiP)[1]. One of the regulatory responses is to synthesize chlorophyll *f*, which absorbs further to red than chlorophyll *a* in a region of the spectrum that is not used under normal light conditions. Once it has been synthesized, the chlorophyll *f* is then incorporated into the antenna systems of Photosystems I and II (PSI and PSII) allowing them to harvest the available light. The pathway by which the chlorophyll *f* synthesis takes place is not well known. However, it has been demonstrated that chlorophyll *f* synthesis depends on the expression of an unusual gene that shows very high sequence homology to one of the two core proteins of PS II [2]. This gene is a so-called “super-rogue” paralog of the *psbA* gene and the associated protein has been named ChlF synthase. Very little is known about the structure and function of the ChlF enzyme but it has been shown that when it is illuminated at low temperature spin-polarized chlorophyll triplet states are observed. This allows the enzyme to be studied using optically detected magnetic resonance (ODMR) data. Fluorescence detected ODMR measurements reveal the presence of several different types of chlorophyll triplet states with different zero-field splitting parameters and optical properties. The triplet-minus-singlet spectrum obtained from absorption detected ODMR is remarkably similar to the spectrum of the triplet state of the primary donor  $^3P_{680}$  of PSII, suggesting that ChlF probably has an electron transfer pathway similar to that of PSII. The ODMR data also reveal the presence of chlorophyll *f* triplet states and carotenoid triplets. These clearly suggest that the enzyme is light activated and has a photoprotection mechanism as well. The site of chlorophyll *f* synthesis remains unknown but the similarity of the data to that of PSII points to the so-called Chl-Z site as a possibility.

[1] F. Gan, S. Zhang, N.C. Rockwell, S.S. Martin, J.C. Lagarias, D.A. Bryant *Science* **345**, 1312-1317 (2014)

[2] M.Y. Ho, G. Shen, D.P. Canniffe, C. Zhao, C., D.A. Bryant *Science*, **353(6302)**, aaf9178 (2016)

## **Porphyrin-based Triad with Exceptionally High MFE on Phosphorescence**

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Magnetic control over molecular emissivity presents interests for various fields of technology and medicine. We present experiments exploring magnetic field effects (MFE) on phosphorescence in donor-acceptor dyads and triads based on Pt porphyrins (PtP). In one triad, consisting of phosphorescent Pt porphyrin (PtP), rosamine B (RosB) and trialkoxybenzene (TAB), covalently linked together by conductive oligophenylene bridges, photoexcitation leads to two sequential reversible electron transfer processes (ET), generating two radical pairs (RP), respectively. The first rate-limiting ET originates in the local PtP triplet state, and it is slightly endergonic, competing with, but not entirely quenching the PtP phosphorescence. The second ET is exergonic, resulting in the formation of the final RP with large inter-radial distance. The RPs recombine either to the ground state (singlet channel) or back to the emissive PtP triplet state (triplet channel). The net distribution of the RP decay over the recombination channels, and hence the phosphorescence decay time and intensity, are governed by the spin dynamics in the RP(s) and are sensitive to magnetic field. The phosphorescence of the triad was found to exhibit remarkably strong positive MFE with the magnitude reaching up to ~12% in the field of a hand-held toy magnet. A kinetic model was developed that allowed us to reproduce the observed behavior of the triad. Overall, this work constitutes an important step towards the design of magnetically sensitive luminescent materials, which in the future may be exploited in construction of a new kind of biological imaging probes.

## **Investigations into chirality and spin-selective redox chemistry**

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I will describe recent studies that investigate the effects of electron spin in electron transfer and electron initiated chemical reactions of supramolecular assemblies and at electrodes. I will discuss how charge polarization and charge transfer in chiral molecules and assemblies is accompanied by spin polarization and spin transfer, because of the chiral induced spin selectivity (CISS) effect. I will report on recent studies which show how the CISS effect modulates electron transfer rates in chiral assemblies and how spin polarized electron currents can be used to be used to enhance the selectivity of electrochemical reactions.

# **Completing the Picture: A $^{13}\text{C}$ -Hyperfine Mapping of Flavin Semiquinone Radicals by Photo-CIDNP NMR**

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In this contribution we present the electronic structure of flavin semiquinone radicals in terms of their  $^{13}\text{C}$  hyperfine coupling constants. Photochemically induced dynamic nuclear polarization (photo-CIDNP) spectroscopy was used to study both the neutral and anionic radical species of flavin mononucleotide (FMN) in bulk aqueous solution. Apart from universally  $^{13}\text{C}$  labelled FMN, partially labelled isotopologues were used to increase sensitivity for nuclei exhibiting very small hyperfine couplings and to cope with spectral overlap. In addition, experimental findings are supported by quantum chemical calculations and implications for the spin density distribution in free flavin radicals are discussed [1]. A comparison with  $^{13}\text{C}$  hyperfine couplings obtained from flavin radicals in protein surroundings will be presented [2].

[1] N. Pompe, B. Illarionov, M. Fischer, A. Bacher, S. Weber. *J. Phys. Chem. Lett.*, submitted

[2] E. Schleicher, S. Rein, B. Illarionov, A. Lehmann, T. Al Said, S. Kacprzak, R. Bittl, A. Bacher, M. Fischer, S. Weber. *Sci. Rep.* **11**, Art. No. 18234 (2021)

## Optimal Illumination for Optical Overhauser DNP

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NMR spectroscopy while offering a wealth of information on molecular structure and dynamics has always suffered from inherently low sensitivity which limits applications, not least in the case of volume-limited biological samples. Several spin chemical mechanisms result in spin polarization which can potentially be used to tackle this challenge, with photo-CIDNP methods based on the radical pair mechanism and parahydrogen based PHIP methods well known. A less explored route is the use of laser pumping to hyperpolarize electrons via the radical triplet pair mechanism (RTPM) which we have previously shown can lead to  $^1\text{H}$  NMR enhancements in solution after Overhauser driven polarization transfer to nuclear spins. Not only does this offer a route to DNP-NMR enhancements in aqueous solution without the technical demands of microwave pumping, but using hyperpolarized electrons means the maximum theoretical enhancements exceed the Boltzmann limited values of microwave pumped Overhauser DNP [1]. Here we show that the attainable NMR signal enhancements are also significantly greater for reduced sample volumes (Fig. 1). While at first glance this may seem problematic due to the reduced filling factor and hence lower sensitivity of NMR detection for small volume samples it does in fact mean that Optical Overhauser DNP is fortuitously well suited to tackle the sensitivity challenge for volume-limited samples.

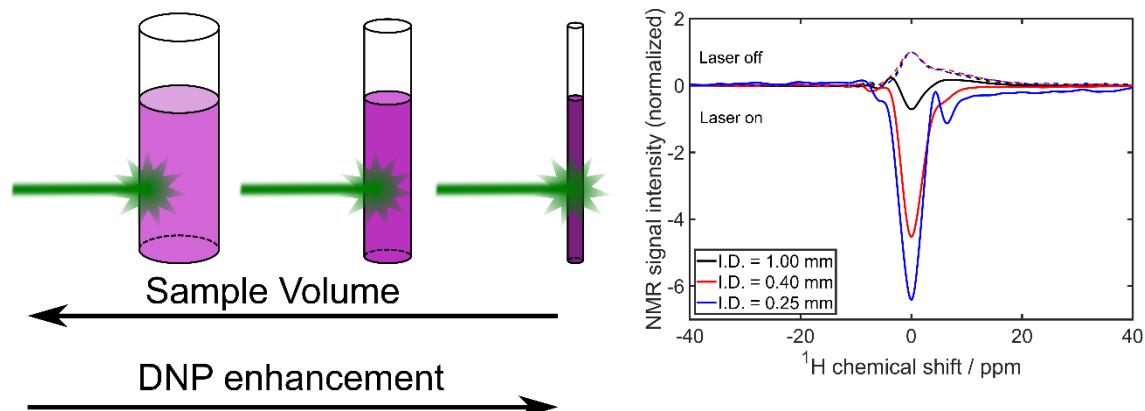


Fig. 1 Reducing the sample tube internal diameter while optimising concentrations of radical and dye leads to increased laser-on vs laser-off DNP enhancement of the  $^1\text{H}$  NMR signal of water. Figure reproduced from [2].

We use numerical simulations to explore the optimal illumination conditions for RTPM based DNP, considering pulsed illumination regimes [3] and showing the now experimentally verified prediction of significant sample volume effects [2]. We show that for low-volume samples simultaneous optimization of coupling and leakage factors in the well-known Overhauser equation is possible and predict even greater enhancement factors in the case of volume optimized NMR detection, adding Optical Overhauser DNP to the growing number of hyperpolarization methods that show potential for integration with microfluidic NMR [4].

### References

- [1] M. W. Dale and C. J. Wedge, *Chem. Commun.*, 52, 13221–13224 (2016).
- [2] D.J. Cheney and C.J. Wedge, *J. Magn. Reson.*, 337, 107170 (2022).
- [3] D.J. Cheney and C.J. Wedge, *J. Chem. Phys.*, 152, 034202 (2020).
- [4] J. Eills, W. Hale and M. Utz, *Prog. Nucl. Magn. Reson. Spectrosc.*, 128, 44-69 (2022).

## Triplet Excited State Reactions at the Surfaces of Colloidal Quantum Dots

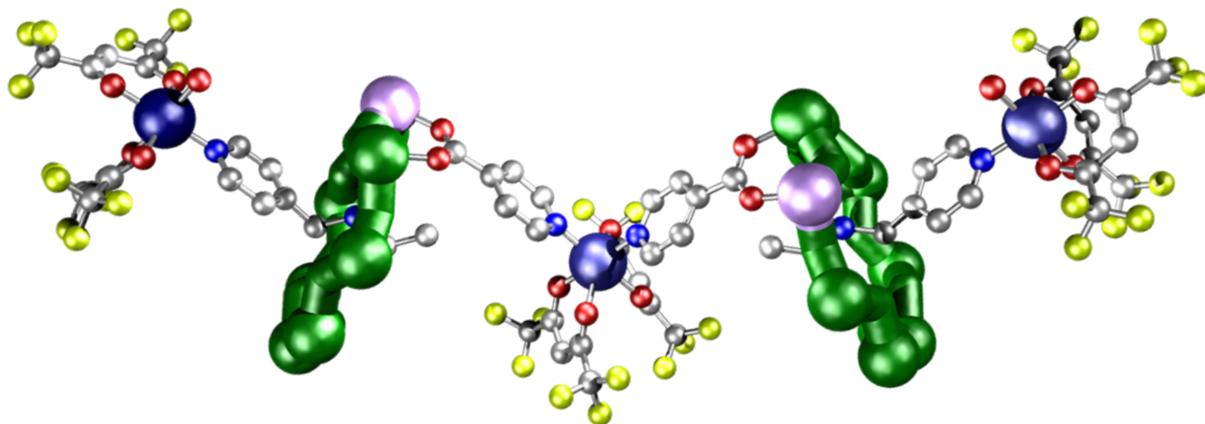
Emily A. Weiss, Northwestern University

The interactions among angular momentum states within the excitonic manifold of colloidal nanocrystals enable the nanocrystals to photocatalyze a greater range of triplet excited state reactions, such as [2+2] photocycloadditions, than organic molecules and metal complexes. The near-zero singlet-triplet splitting in cadmium chalcogenide QDs allows formation of high-energy triplet states without accompanying high electrochemical potentials that trigger side reactions. Here we explore the mechanisms by which the photophysics of the crystalline cores of quantum dots and nanoplatelets combine with the chemistry at their surfaces to enable selective organic reactions from triplet excited state precursors.

## Making supramolecular assemblies that could be used in quantum information processing

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Around fifteen years ago it was proposed that molecular magnets could be used as qubits for quantum information processing.<sup>1,2</sup> Many groups focused on demonstrating that coherence times can be extended by chemical control.<sup>3</sup> The major advantage that molecules possess over other proposed hardware is the potential to control inter-spin interactions.



We are pursuing chemistry to link together heterometallic rings to make large supramolecular structures that bring together multiple such potential qubits. In some cases, we can include switchable units that allow us to propose strategies to implement entangling gates such as the CNOT or the  $\sqrt{iSWAP}$  gate.<sup>4</sup> In other cases we have attempted to build supramolecules that could include quantum error correction,<sup>5</sup> and or could model decoherence in quantum teleportation.<sup>6</sup>

### References

1. M. Leuenberger and D. Loss, *Nature* 2001, **410**, 789.
2. F. Meier, J. Levy, and D. Loss, *Phys. Rev. Lett.* 2003, **90**, 47901.
3. Bader *et al.*, *Nature Commun.*, 2014, **5**, 5304; Zadrozny *et al.*, *J. Amer. Chem. Soc.* 2014, **136**, 15841; Atzori *et al.*, *J. Amer. Chem. Soc.* 2016, **138**, 2154; Pedersen *et al.*, *J. Amer. Chem. Soc.* 2016, **138**, 5801; Ariciu *et al.*, *Nature Commun.* 2019, **10**, 3330; De Camargo *et al.* *Angew. Chem. Int. Ed.* 2021, **60**, 2588.
4. J. Ferrando-Soria *et al.*, *Nature Commun.*, 2016, **7**, 11377;
5. S. Lockyer *et al.*, *Chem. Sci.*, 2021, **12**, 9104.
6. S. Lockyer *et al.*, manuscript submitted.

## **Fluorescence Microscopy of Cyclic Radical Pair Based Photochemical Reactions**

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Fluorescence microscopy comprises a large number of very sensitive and flexible methodologies with a wide range of applications in many fields including biology and nanoscience. In recent years, fluorescence microscopy has been applied as a tool to study cyclic photochemical reactions, in particular those of flavins [1,2], which proceed through the formation of radical pair intermediates. Under continuous photoexcitation, such reactions create an equilibrium between the chromophore-containing precursor ground state and the radical pair. If the ground state molecule can also undergo fluorescence on photoexcitation, then the amount of fluorescence emitted depends on the position of this equilibrium. As the ratio of radical pairs returning to the ground state through spin-selective reaction (fast) and non-spin selective reaction (slow) can be influenced using static and / or oscillating magnetic fields, the fluorescence intensity can be used to probe the radical pair dynamics. Indeed, we have recently demonstrated magnetic field responses in the natural autofluorescence of living cells using this approach [3].

Fluorescence microscopy of radical pair based cyclic reactions is a method with important applications in studying biological magnetosensitive processes, in investigating the spin-dynamics of radical pairs at very low concentrations (including individual radical pairs [4]), and for developing and applying magnetic field sensor probe molecules for use in biosensing. In this lecture we present our group's most recent progress in the development and application of fluorescence-based microscopy to radical pair processes, considering instrumental and theoretical aspects, along with the development and applications of model reaction systems.

### **References:**

- [1] C. A. Dodson *et al.*, *Chem. Commun.*, **51**, 8023-8026 (2015)
- [2] V. Déjean *et al.*, *Chem. Sci.*, **11**, 7772-7781 (2020).
- [3] N. Ikeya and J. R. Woodward, *PNAS*, **118** (3), e2018043118 (2021).
- [4] N. Ikeya, *et al.*, *Mol. Phys.* DOI: 10.1080/00268976.1559954 (2018).

## Triplet Dynamic Nuclear Polarization of Bio-relevant Molecules

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Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) are powerful and versatile methods in modern chemistry and biology fields. Nevertheless, they suffer from intrinsically limited sensitivity due to the low nuclear spin polarization at ambient temperature. One of the promising methods to overcome this limitation is dynamic nuclear polarization (DNP) that transfers spin polarization from electrons to nuclei. In particular, DNP based on photo-excited triplet (triplet-DNP) is promising, since it allows the hyperpolarization at room temperature.<sup>1-3</sup> In typical scheme of triplet-DNP, the spin-selective intersystem crossing (ISC) produces the large electron spin polarization in the excited triplet state sublevels, and this polarization is effectively transferred to nuclear spins by a microwave irradiation for satisfying Hartmann-Hahn condition, so-called integrated solid effect (ISE).

While much efforts have been devoted to obtaining the large nuclear polarization based on triplet-DNP, the application of triplet-DNP has been limited to nuclear physics experiments. Towards biological applications, we have proposed to introduce materials chemistry into the field of triplet-DNP,<sup>4</sup> which realizes the hyperpolarization of drug molecules in nanoporous metal-organic frameworks (MOFs)<sup>5,6</sup> and the polarization transfer from nanocrystals to water.<sup>7,8</sup>

### References

- <sup>1</sup>A. Henstra *et al.*, *Chem. Phys. Lett.*, **165**, 6-10 (1990).
- <sup>2</sup>K. Takeda, Triplet State Dynamic Nuclear Polarization: Basics, Concepts, Methods, VDM Publishing (2009).
- <sup>3</sup>K. Tateishi *et al.*, *Proc. Natl. Acad. Sci. U. S. A.*, **111**, 7527-7530 (2014).
- <sup>4</sup>K. Nishimura *et al.*, *Chem. Commun.*, **56**, 7217-7232 (2020).
- <sup>5</sup>S. Fujiwara *et al.*, *J. Am. Chem. Soc.*, **140**, 15606-15610 (2018).
- <sup>6</sup>S. Fujiwara *et al.*, *Angew. Chem. Int. Ed.*, **61**, e202115792 (2022).
- <sup>7</sup>K. Nishimura *et al.*, *Phys. Chem. Chem. Phys.*, **21**, 16408-16412 (2019).
- <sup>8</sup>N. Matsumoto . *et al.*, *ChemRxiv*, DOI: 10.26434/chemrxiv-2022-zrnh5 (2022).

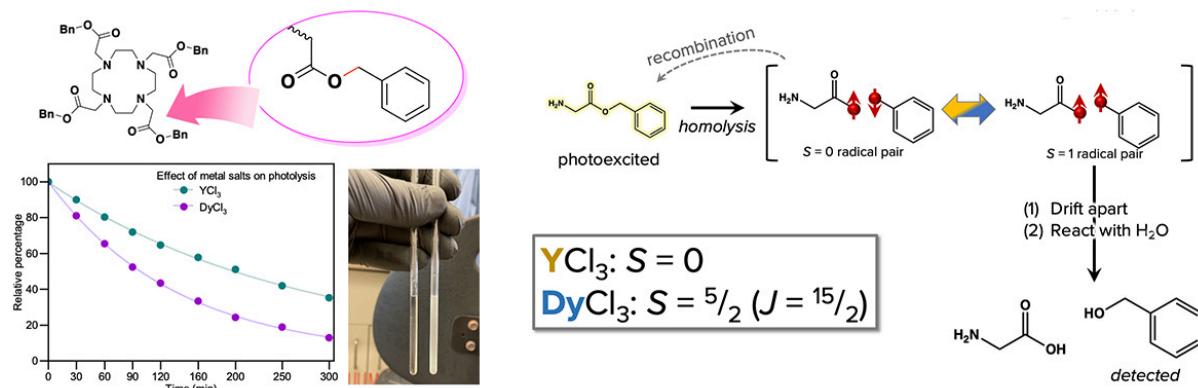
## Rare-Earth Magnetic Control of Photolysis Reactions

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Rare-earth elements are essential in modern technology. Yet, their chemical separations and purification is a complicated procedure because the typical thermodynamic quantities (e.g. solubility or ionic radius) vary only gradually, producing inefficient separations processes. Magnetic properties, in contrast, vary starkly across the rare-earth elements, and developing means of harnessing magnetism to separate them is of prime importance.

In this talk, we will cover our approach to harnessing the electronic spin of the rare-earths for a reactive separations procedure that exploits a magnetic effect on radical-pair reactions<sup>1</sup> for the separations handle. Turro and coworkers, as well as Sakaguchi, showed three decades ago that rare earths can modify the outcomes of chemical reactions that incorporate these radical pairs.<sup>2,3</sup> Yet the exact magnetic parameters responsible for that control e.g. spin ground state, bulk magnetic moment, or spin relaxation time, among others, are still undefined.

We are currently designing ligand shells to both provide that understanding and enable tests of chemical separations. We are specifically targeting predominantly O- and N-atom donor chelate backbones, with radical-pair forming groups appended to them. As an initial proof of concept, we are studying the role that magnetic rare earths play in governing the photolysis of benzyl esters, specifically benzylglycine, which will comprise the radical-pair forming groups we eventually append to the ligand scaffolds (**Fig. 1**). Results in this area will be discussed.



**Fig. 1.** Summary of results, target chemical system, and spin catalysis.

### References.

- [1] Steiner U. et. al., *Chem. Rev.* **89**, 51 (1989)
- [2] Turro N. et. al., *Chem. Phys. Lett.* **120**, 397 (1985)
- [3] Sakaguchi, Y. et. al., *Chem. Phys. Lett.* **106**, 420 (1984)
- [4] Buchachenko, A. et. al., *Chem. Rev.* **102**, 603 (2002)

**Spin dynamics simulation package  
for fixed-geometry charge-  
separated systems**

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Charge-separated radical intermediates of photoinduced chemical reactions with rather rigid molecular geometry and strong coupling between unpaired electrons participate in various important processes, for example, in photosynthesis of plants [1]. It is tempting to construct an artificial organic photosynthetic system which is mimicking the processes in the natural one to tackle the world's growing energy consumption challenge in a "green" way. This requires deep understanding of photochemical processes taking place both in natural and artificial systems. Both coherent and incoherent spin selective processes strongly affect the chemical properties of such charge-separated states, thus modulating the efficiency of the overall processes [2], but sometimes it is difficult to separate the influence of different processes involved. Experimental methods developed in spin chemistry: magnetic field affected reaction yield (MARY), chemically induced electron and nuclear polarization (CIDEP and CIDNP, correspondingly) can be applied to disentangle contributions from different channels, but they are effective only in combination with thorough analytical and numerical calculations.

In this contribution, the newly written Matlab based script package will be introduced, which allows to calculate the magnetic field effect of any observable, including CIDNP [3], CIDEP, MARY [4], and is freely available on request. It has been successfully applied for simulating proton and carbon-13 solution-CIDNP field dependences of a series of donor-linker-acceptor systems with at least 23 magnetic nuclei with non-zero hyperfine coupling in charge-separated state [3]. Its architecture and approximations made will be described, and the influence of model parameter's variations will be shown.

This work has been supported by the Russian Science Foundation (project 20-63-46034).

**References**

- [1] K. Möbius, *Chem. Soc. Rev.* **29**, 129 (2000)
- [2] J. Schäfer *et al.*, *Phys. Chem. Chem. Phys.* **20**, 27093 (2018)
- [3] I. Zhukov *et al.*, *J. Chem. Phys.* **155**, 224201 (2021)
- [4] D. Mims *et al.*, *Science*, **374**, 1470 (2021).



**Simulating radical pair magnetoreception in IBM's quantum computer.**

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Most studies on the simulation of radical pairs use classical computation techniques to solve the quantum master equation[1-5]. Although efficient, these techniques do not scale well for large numbers of atoms and can have long computation times. We propose a technique that uses quantum computation to simulate the interactions as a noisy channel, employing the mapping of spin  $\frac{1}{2}$  particle system into qubits. It improves the computation and results in a more realistic simulation. We extend the technique to simulate higher spin systems in quantum computers using Clebsch-Gordan coefficients to define a set of qubits as bosons or fermions. The simulations were programmed in QISKit and tested in IBM's quantum computers and simulators.

These techniques can be used to simulate open quantum systems and spin chemistry faster and with more precision[6-8], as quantum computers are best fit for simulations of quantum interacting systems.

**References**

- [1] Carrillo et al. Environment Induced anisotropy and sensitivity of the radical pair mechanism in the avian compass. *Phys. Rev. E*, 92:012720. (2015).
- [2] Fay et al. How quantum is radical pair magnetoreception? *Faraday Discussions*, 221:77–91. (2020).
- [3] Hiscock et al. Navigating at night: fundamental limits on the sensitivity of radical pair magnetoreception under dim light. *Quarterly Reviews of Biophysics*, 52. (2019).
- [4] Hiscock et al. The quantum needle of the avian magnetic compass. *Proceedings of the National Academy of Sciences*, 113(17):4634–4639. (2016).
- [5] Hore and Mouritsen. The radical-pair mechanism of magnetoreception. *Annual Review of Biophysics*, 45(1):299–344. PMID: 27216936. (2016).
- [6] Knill, E. Quantum computing. *Nature* 463, 441–443 (2010)
- [7] N Cody Jones et al *New J. Phys.* 14 115023 (2012).
- [8] Dong-Sheng Wang, Dominic W. Berry, Marcos C. de Oliveira, and Barry C. Sanders. Solovay-Kitaev decomposition strategy for single-qubit channels. *Phys. Rev. Lett.* 111, 130504 (2013).

## Magnetic field effect-based fluorescence fluctuation spectroscopy

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Scientists from different fields, ranging from spin chemists to behavioural biologists, have conducted much research to unravel the mystery of animal magnetoreception [1]. However, an experiment is needed to establish whether cryptochromes can function as magnetoreceptors in living cells. A transient absorption-based microspectroscopy was developed for such a purpose [2], however, to fully understand the complex mechanisms taking place in living cells a step in a new direction is required. One such approach is fluorescence fluctuation spectroscopy (FFS), which monitors the fluctuations of fluorescence intensity from a femtolitre volume within the sample. Monitoring these fluctuations can provide information on, for example, the number of molecules, diffusion coefficients, protein binding, and protein-protein interactions [3]. To this end, we have developed a unique magnetic field effect (MFE)-based FFS confocal microscope for investigating cellular proteins at the single-molecule level.

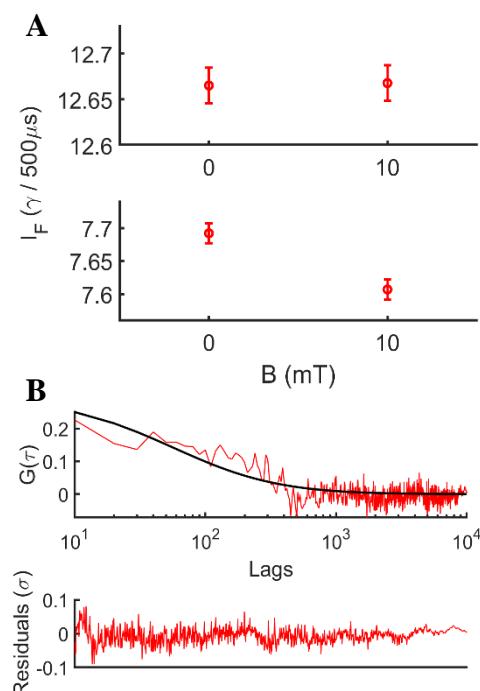
As a proxy for cryptochrome, the protein-ligand complex HEWL (hen-egg white lysozyme)-FMN (flavin mononucleotide) was examined. We applied a magnetic field “on-off” regime on the blue-light induced fluorescence captured with a single-photon avalanche diode (SPAD). The ultra-high sensitivity of this single-photon detector is exemplified by the data shown in Fig. 1A, with an MFE of ~1 % measured on a ~7 photon level fluorescence signal. An experimental confocal volume of 0.54 fL (Fig. 1B) suggests we are observing MFEs on 65-molecules. Experiments including, magnetic field effects, fluorescence correlation spectroscopy, and fluorescence anisotropy will be presented and discussed.

### References

- [1] P. J. Hore and H. Mouritsen, *Ann. Rev. Biophys.*, **45**, 299-322 (2016).
- [2] J. P. Beardmore, L. M. Antill et al., *Angew. Chem. Int. Ed.*, **54**, 8494-8497 (2015); L. M. Antill et al., *Rev. Sci. Instrum.*, **89**, 023707 (2018).
- [3] D. M. Jameson *et al.*, *Biophys. Rev.*, **1**(3), 105 (2009).

### Acknowledgements

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**Figure 1:** **A.** Magnetic field effects with SPAD detection. (Top) FMN (200 nM), (bottom) FMN (200 nM) + HEWL (0.5 mM) emission between 500-600 nm. **B.** FCS on rhodamine 110 (10 nM) yielding an effective number of molecules,  $N$ , of 3.4.



## Using Chemistry to Design and Synthesize New Maser Gain Media

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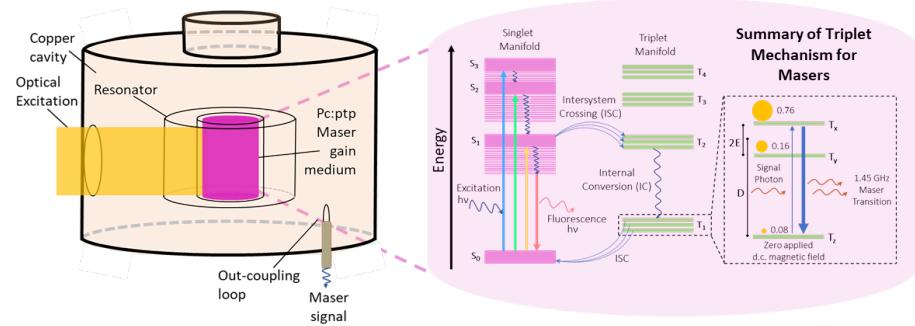
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Microwave-based quantum sensors are currently inexpedient at room temperature due to thermally derived “noise” microwave photons. However, a promising class of ultralow-noise microwave amplifiers can be engineered by exploiting particular materials that exhibit a strong electron spin polarization (ESP), such as photoexcited pentacene-doped p-terphenyl (pc:ptp)(1) and NV<sup>-</sup> diamond(2). These devices operate through microwave amplification by stimulated emission of radiation (maser) and multiply extremely weak signals by several orders of magnitude. Yet, before we apply these devices to quantum technologies, improvements are required that actively remove thermal noise prior to masing, boost the amplification gain, and dulcify the necessary operating conditions.

Taking pc:ptp as the archetype organic solid-state maser system, we have employed a chemical design approach to tune the properties of maser candidate molecular systems. We have synthesized several new triplet and radical-based materials to act as potential maser gain media and analyzed their performance to understand the link between their electron spin dynamics and their merit for inclusion in future maser devices. Our new materials demonstrate the capacity to operate at various resonant frequencies and can be optically pumped at more easily generated wavelengths, potentially representing a significant enhancement in the utility of masers as tools in future applications.



## References

- [1] H. Wu *et al.*, *Opt. Express.* **28**, 29691 (2020).
- [2] J. D. Breeze *et al.*, *Nature*. **555**, 493–496 (2018).

**Pentacene Bi-radical Nitroxides studied via  
Transient EPR and Transient Absorption Spectroscopy**

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The ability to generate large electron spin polarization optically is useful for many applications including magnetometry, high-energy physics studies, molecular spintronics and magnetic resonance spectroscopy. Pentacene-radical derivatives have previously been shown to produce spin polarization on the tethered radical via an enhanced intersystem crossing optical pathway[1]. However, the mechanism leading to the observed spin polarization depends on many factors, such as the radical substituent, the choice of linker, and the different substituents on the pentacene moiety. The ability to tune the spin polarization, lifetimes and optical pathway of chromophore systems via selective tuning of molecular substituents is of considerable interest [2,3]. In this work we use CW EPR, transient EPR, transient absorption and UV-visible spectroscopies to investigate a pentacene mono-nitroxide and a bi-nitroxide system that have been synthesized with a short alkyne linker to produce a large exchange coefficient between the pentacene and radical systems. We find that upon optical excitation of the pentacene-radical systems a pentacene triplet is not observed to form in either system. Instead, in both cases, the pentacene ground-state bleach signal appears to persist for a shorter amount of time than the singlet photoinduced absorption, indicative of another state being populated with a similar absorption at 500-510 nm to the initially populated singlet state. In addition, we observe that the excited state associated with this absorption decays more rapidly in the case of the bi-radical pentacene molecule when compared to the mono-radical pentacene. Transient EPR measurements are currently underway to aid in identifying the long-lived state.

## References

- [1] Avalos, C. E., Richert, S., Socie, E. , Karthikeyan, G., Casano, G., Stevanato, G., Kubicki, D. J., Moser, J. E., Timmel, C. R., Lelli, M, Rossini, A. J., Emsley, L., Ouari, O. *J. Phys. Chem. A*, 2020, 124, 6068-6075.
- [2] Wasielewski, M.R., Forbes, M.D.E., Frank, N.L., Kowalski, K., Scholes, G. D. Yuen-Zhou, J., Baldo, M. A., Freedman, D. E., Goldsmith, R. H., Goodson III, T., Kirk, M. L., McCusker, J. K.. Ogilvie, J. P., Shultz, D. A., Stoll, S., Whaley, K. B. *Nat Rev Chem* 4, 490–504 (2020).
- [3] Kundu, K., Duborca, T., Rane, V., Mentink-Vigier F. *J. Phys. Chem. A* 2022, 126, 16, 2600–2608



## Magnetic field effects on radical pair reactions: estimation of B<sub>1/2</sub> for the flavin-tryptophan radical pair in cryptochrome

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Due to the influence of spin-selective reactivity, relatively slow spin relaxation, and electron-nuclear hyperfine interactions, the yields of the reaction products of short-lived radical pair intermediates,  $\Phi(B)$ , are frequently found to depend sigmoidally on the strength of an applied magnetic field, B [1]. This behaviour is often characterised by a parameter, B<sub>1/2</sub>, defined as the magnetic field at which  $\Phi(B)$  is mid-way between the reaction yield at zero field and the “saturation” value at high field:

$$\Phi\left(B_{\frac{1}{2}}\right) = \frac{1}{2}[\Phi(0) + \Phi(\text{high field})].$$

While B<sub>1/2</sub> is principally dependent on the hyperfine interactions in the radicals, its value is also influenced by factors including reaction kinetics, spin relaxation and electron exchange and dipolar interactions [2]. Accurate estimation of the hyperfine contribution to B<sub>1/2</sub> is valuable as a means to extract information on these additional factors from experimental data.

Here we implement a number of methods for simulating the magnetic field response and consequently estimating B<sub>1/2</sub> for a flavin-tryptophan radical pair in cryptochrome, the putative biological sensor behind the avian magnetic compass sense [3]. We compare results obtained using different simulation methods with the empirical Weller equation [4], commonly used to estimate B<sub>1/2</sub>. Weller’s expression for B<sub>1/2</sub> is found to only be applicable to small, short-lived, rapidly tumbling radicals in solution, with limited reliability otherwise.

### References

- [1] Steiner, U. E. and T. Ulrich. 1989. Magnetic field effects in chemical kinetics and related phenomena. Chem. Rev. 89: 51-147
- [2] Maeda, K. et al. 2012. Magnetically sensitive light-induced reactions in cryptochrome are consistent with its proposed role as a magnetoreceptor. Proc. Natl. Acad. Sci. USA, 109: 4774-4779
- [3] Hore, P. J., and H. Mouritsen. 2016. The radical pair mechanism of magnetoreception. Annu. Rev. Biophys. 45:299-344
- [4] Weller, A., F. Nolting, and H. Staerk. 1983. A quantitative interpretation of the magnetic-field effect on hyperfine-coupling-induced triplet formation from radical ion-pairs. Chem. Phys. Lett. 96:24-2

## Theory of Nuclear Spin Dependent Enzymatic Synthesis of ATP *in vivo* in Strong Magnetic Fields

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Synthesis of ATP (adenosine triphosphate – the main source of energy in all living organisms) has been proved to be  $^{25}\text{Mg}$  nuclear spin dependent process *in vitro* and *in vivo* [1-4]. Well known HFI mechanism of singlet-triplet conversion of ion-radical pairs is able to explain magnetic field dependencies of ATP synthesis in low magnetic fields, however, is not able to explain ones in strong magnetic fields  $B \sim 80$  mT.

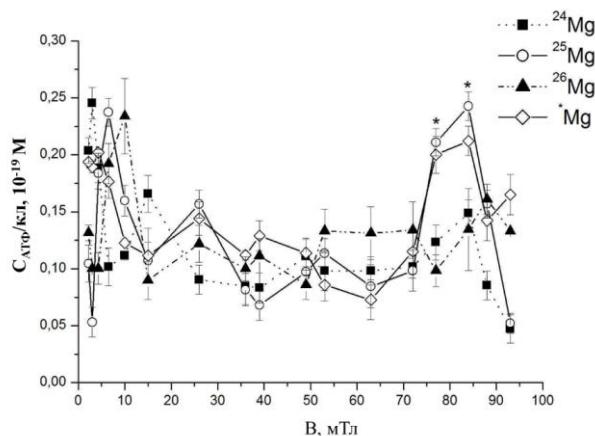


Fig. 1. Magnetic field dependences of intracellular ATP content in *E. coli* bacteria grown on M9 medium with magnesium isotopes  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ ,  $^{26}\text{Mg}$  and natural magnesium Mg. The data is given per cell. The range of magnetic fields is 0.8-98 mT.

To explain those effects a new model and a theory of S-T conversion for equivalent electron spins interacting with a nuclear spin was proposed. This S-T conversion was shown to be inevitably accompanied by redistribution of charge density decreasing Coulomb repulsion of interacting particles. Theoretical results qualitatively coincide with the experimental ones for ATP production in bacterial cells *Escherichia coli*.

- [1] Buchachenko A.L. *Magnetic Isotope Effect in Chemistry and Biochemistry*. (Nova Science Publishers, New York) 2009.
- [2] Buchachenko A.L. *Magneto-Biology and Medicine*. (Nova Science Publishers, New York) 2014.
- [3] Letuta U.G., Avdeeva E.I. Magnetic-dependent ATP pool in *Escherichia coli* // *Doklady Biochemistry and Biophysics*, **474**(1), 196, (2017)
- [4] Letuta U.G., Berdinskiy V.L., Udagawa C., Tanimoto Y. Enzymatic mechanisms of biological magnetic sensitivity // *Bioelectromagnetics*, **38**(7), 511, (2017).
- [5] Letuta U.G. Magnesium magnetic isotope effects in microbiology // *Archives of Microbiology*, Published: 21 February 2021 (2021)

## New light-induced Pulsed ESR Dipolar Spectroscopy methodologies for the elucidation of molecular conformation

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The suitability of the photoexcited triplet state of porphyrins for nanometer distance measurements by Pulsed ESR Dipolar Spectroscopy (PDS) was demonstrated in combination with nitroxide radicals. Thanks to its non-Boltzmann population, the photoexcited triplet enhanced signal intensity when used as detection spin in DEER [1] and improved modulation depth when used as pump spin in LaserIMD [2]. Here we exploit the orientation selection effects in these triplet–nitroxide experiments to extract additional conformational information in model peptides with different chromophores, namely tetraphenylporphyrin, diiodo-BODIPY and Erythrosin B (Fig. 1 (a)) [3]. Using simulations and DFT calculations, we extract distance distributions and relative orientations of the two spin-bearing moieties, allowing the dominant conformation of the peptide in frozen solution to be identified. We also present, for the first time, a frequency-correlated version of LaserIMD, which monitors the complete orientation dependence of the system in a single experiment.

Going a step further in light-induced PDS, we present the new technique of Light-Induced Triplet-Triplet Electron Resonance spectroscopy (LITTER) [4], which uses photoexcited triplet states as both detection and pump spins, enabling both the distance and angular distributions between the two triplet moieties to be determined in a model peptide (Fig. 1 (b)). LITTER removes the requirement of current light-induced PDS techniques to have a permanent paramagnetic moiety, becoming more suitable for in-cell applications and potentially giving access to distance determination in unmodified macromolecular systems containing photoexcitable moieties. LITTER also has the potential to enable direct comparison with FRET and combination with microscopy inside cells.

- [1] M. Di Valentin *et al.*, *J. Am. Chem. Soc.* **136**, 6582–6585 (2014).
- [2] C. Hintze *et al.*, *J. Phys. Chem. Lett.* **7**, 2204–2209 (2016).
- [3] A. Bowen *et al.*, *J. Phys. Chem. Lett.* **12**, 3819–3826 (2021).
- [4] A. Bertran *et al.*, *J. Phys. Chem. Lett.* **12**, 80–85 (2021).

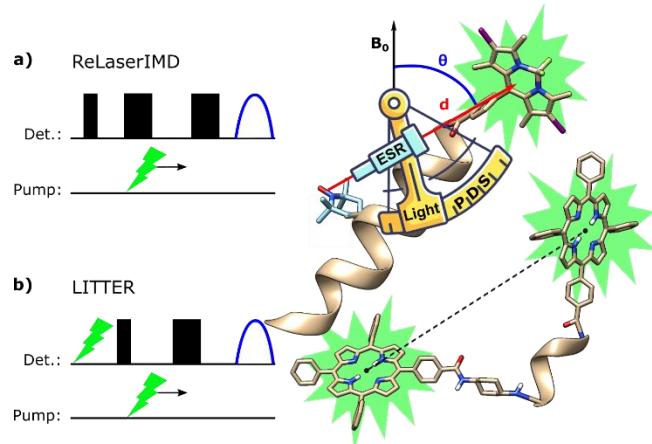


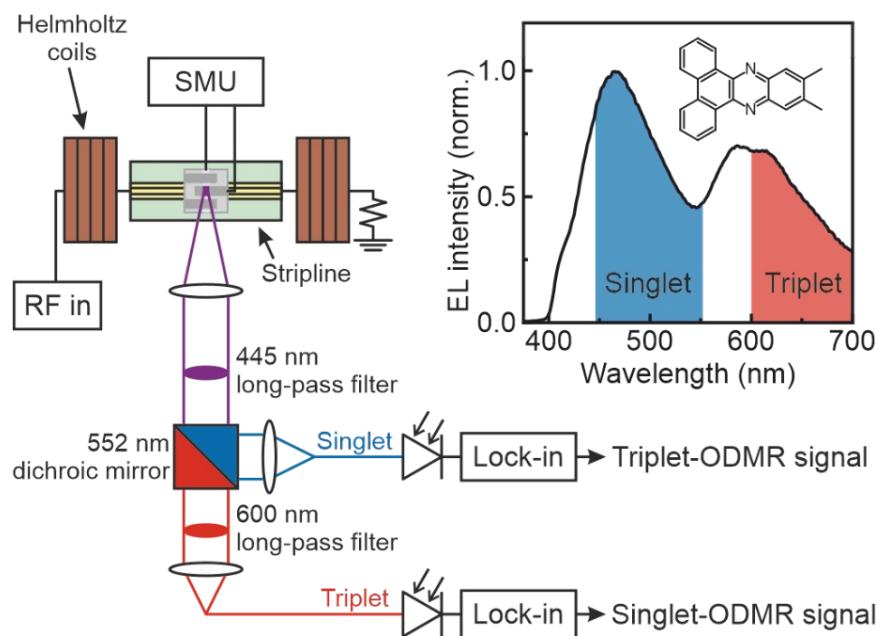
Figure 1. Pulse sequences for the Refocused LaserIMD (a) and LITTER (b) experiments, and structures of model peptides used in the studies of the orientational effects.



# Probing quenching of triplet excitons by charge carriers in dual-emitter OLEDs by phase-sensitive magnetic resonance

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OLEDs exhibit strong sensitivity to magnetic fields due to spin-dependent electron-hole recombination. Employing a dual singlet-triplet emitting guest:host system, we can optically assess the spin-permutation symmetry of charge-carrier pairs by their magnetic-field dependent electroluminescence (EL) as illustrated in the figure [1]. Furthermore, due to the dual-emitting property of the material system used, we gain access to both singlet- and triplet-like states, allowing us to distinguish between singlet-triplet pair interconversion [2] and carrier-exciton quenching [3] processes.



We monitor the interconversion between singlet-like and triplet-like carrier-pair populations in the EL under electron paramagnetic resonance (EPR) conditions and observe deviations from the anticipated anticorrelation in the formation yields of singlet-like and triplet-like carrier pairs. We rationalize the optically detected magnetic resonance (ODMR) spectra using stochastic Liouville simulations of the spin-pair density matrix, based on an interplay between the conventional radical-pair model and an exciton-quenching mechanism. We exploit the extraordinary phase sensitivity of the lock-in quadrature detection technique used to gain insight into the temporal dynamics of the generation and recombination of the molecular triplet states. Using this approach, we observe a non-trivial phase dependence of the ODMR, revealing a dynamic interaction between host and guest molecule triplets.

## References:

- [1] W. Ratzke *et al.*, *Phys. Rev. Appl.* **9**, 054038 (2018)
- [2] U. E. Steiner and T. Ulrich, *Chem. Rev.* **89**, 51 (1989)
- [3] V. Ern and R. E. Merrifield, *Phys. Rev. Lett.* **21**, 9 (1968)

## Concept and experimental demonstration of using a cold load to improve the SNR of an EPR spectrometer

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We describe the concept of using a cold load, connected to the microwave cavity of an EPR spectrometer, to extract thermal noise from the microwave cavity based on the second law of thermodynamics. Our experimental setup successfully demonstrates how **the signal-to-noise ratio (SNR) of the trace from a time-resolved EPR spectrometer can be significantly improved by this technique**. The thermal noise in our spectrometer's microwave cavity is reduced by at least 6 dB (equivalent noise temperature from 290K cooling down to 90K), thus improving the SNR and/or scanning speed. Come to the poster and learn more!

## Sensitive Detection of Magnetic Field Effects in Avian Cryptochromes

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It is well established that certain avian species can harness the Earth's magnetic field, through a process known as magnetoreception, in order to navigate during long range migration. While the natural phenomenon of avian migration is fairly understood, the biophysical process by which it is achieved is still in dispute and offers an intriguing area for research.

The radical pair mechanism (RPM) is a theoretical model put forward by Schulten *et al.*<sup>1</sup> suggesting that spin correlated radical pairs could act as a biological compass. The RPM and behavioural studies that show avian magnetoreception is strongly dependant on the wavelength of light the bird is exposed to, have led to the proposition that photosensitive proteins, known as cryptochromes, located within in the retina of migratory birds are able to act as the source of magnetoreception. Testing the cryptochrome-based RPM hypothesis is by no means trivial as the proposed photocycle has kinetics steps ranging from seconds to picosecond and, as such, a wide and diverse range of experiments are required. Furthermore, the study of magnetically sensitive processes demand that highly sensitive spectroscopic techniques be utilised in order to detect the very small changes in the concentration of the chemical species within the RPM.

Cavity enhanced absorption spectroscopy (CEAS) has been shown to be an ideal candidate for probing the cryptochrome RPM.<sup>2</sup> Here, we present the results of Cavity Ring-down Spectroscopy (CRDS) studies on Avian cryptochromes. CRDS is a nanosecond pump-probe experiment that utilises a tunable laser to scan over many wavelengths and an optical cavity to increase sensitivity. Due to its pulsed nature CRDS is able to detect spectral changes with sub-microsecond temporal resolution. The sensitivity of CRDS, as well as its ability to probe at short timescales makes it an invaluable technique for investigating the cryptochrome RPM.

### References

- [1] Schulten, K., Swenberg, C. E., & Weiler, A. (1978). A Biomagnetic Sensory Mechanism Based on Magnetic Field Modulated Coherent Electron Spin Motion. *Zeitschrift fur Physikalische Chemie*, 111(1), 1-5.
- [2] Xu J, Jarocha LE, Zollitsch T, Konowalczyk M, Henbest KB, Richert S, Golesworthy MJ, Schmidt J, Déjean V, Sowood DJC, Bassetto M, Luo J, Walton JR, Fleming J, Wei Y, Pitcher TL, Moise G, Herrmann M, Yin H, Wu H, Bartölke R, Käsehagen SJ, Horst S, Dautaj G, Murton PDF, Gehrkens AS, Chelliah Y, Takahashi JS, Koch KW, Weber S, Solov'yov IA, Xie C, Mackenzie SR, Timmel CR, Mouritsen H, Hore PJ. Magnetic sensitivity of cryptochrome 4 from a migratory songbird. *Nature*. 2021 Jun;594(7864):535-540.



## Anisotropic Magnetic Field Effects in Cryptochrome Crystals

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Many animals, and in particular migratory birds, have the ability to use the geomagnetic field to navigate [1]. The leading hypothesis to explain the origin of their compass sense is based on magnetosensitive radical pairs (RPs) formed in cryptochrome flavoproteins [1].

Numerous studies have demonstrated that the reactivity of light-induced RPs within flavin-based model systems and cryptochromes could be affected by applied magnetic fields, giving rise to so-called magnetic field effects (MFEs) [2]. Additionally, several theoretical studies have suggested that the flavin/tryptophan radical pair in cryptochromes could also detect the direction of the magnetic field [1], which provides critical information for navigation [3].

Yet, experimental evidence of such compass behaviour is lacking. To date, only an artificial model system, a carotenoid-porphyrin-fullerene triad, has been shown to exhibit anisotropic MFEs, *i.e.* a directionally dependent response to the field [4]. Therefore, any experimental demonstration of the cryptochromes' ability to develop such effects would provide substantial support to the radical pair hypothesis of avian magnetoreception.

This contribution endeavours to assess the ability of cryptochromes to exhibit an anisotropic field response. Such a response can only develop if the radicals are somewhat immobilised and oriented. *In vivo*, it has been suggested that this could be achieved via binding to interaction partners associated with cell membranes [1]. Here, we explore the use of direct molecular alignment and immobilisation via protein crystallisation, and examine the response of cryptochrome crystals to a rotating field by confocal microscopy.

We report that, under continuous photoexcitation, the fluorescence intensity of *Drosophila melanogaster* cryptochrome crystals is modulated by the direction of the field. This demonstrates the ability of cryptochromes to behave as chemical compasses and carries strong implications regarding the viability of a cryptochrome-based avian compass.

[1] P. Hore and H. Mouritsen, *Annu. Rev. Biophys.* **45**, 299 (2016)

[2] E. Evans *et al.*, *Interface Focus* **3**, 20130005 (2013)

[3] W. Wiltschko and R. Wiltschko, *Science* **176**, 62 (1972)

[4] C. Kerpel *et al.*, *Nat. Comm.* **10**, 3707 (2019)

# Designing Magnetic Superstructures in Vacuum Deposited Phthalocyanine Thin Films

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Phthalocyanines are a class of polyaromatic molecules presenting favourable optical, physical and electronic properties for a plethora of technological applications. This includes optoelectronics, spintronics, as well as quantum information processing [1]. Production of phthalocyanines as molecular thin films is a novel approach toward such applications with greater device compatibility, where further development and understanding of interactions between deposited molecules and at the substrate interface are needed for reliable production.

The macrocyclic structure of phthalocyanines allows coordination to a wide range of transition metal ions or functional groups via core nitrogen atoms. This, combined with their ability to self-assemble into ordered structures has a significant effect on physical properties, altering charge transfer, as well as critically influencing magnetic properties of the molecule and film [2]. Isolated spin-active phthalocyanines have been diluted in different diamagnetic host matrices, exhibiting long-lived spin coherence lifetimes for quantum information processing [3]. Vanadyl phthalocyanine (VOPc) in particular has been shown to demonstrate coherent spin-manipulation up to room temperature as frozen solutions and crystalline dispersions [4]. Control of molecular orientation and ferromagnetism has been shown for iron phthalocyanine (FePc) systems for magneto-optical and spintronic devices [5].

In this work, vacuum deposition is employed to reliably deposit high purity mixed thin films of non-planar vanadyl phthalocyanine and planar iron or zinc phthalocyanine (FePc/ZnPc). By selectively utilising combinations of spin-active and diamagnetic phthalocyanines in a controlled stoichiometry, regimes with favourable magnetic and conductive properties for spintronic and quantum information processing applications can be obtained. Composition and molecular orientation are varied, where superstructures of alternating or isolated spin-active phthalocyanines occur with direct exchange or hyperfine coupling respectively. Coordination of metal ions with the oxide moiety of VOPc is used as a potential driving force for ordering between the two species and formation of superstructures. Electron paramagnetic resonance (EPR) spectroscopy is utilised to investigate magnetic properties of isolated spins, where orientation-dependent microwave interactions are related to grazing-incidence wide angle x-ray scattering (GIWAXS) measurements. Orientation dependent direct magnetic exchange interactions are studied through superconducting quantum interference device (SQUID) magnetometry. Choice of different transition metal ions provides the opportunity to help build methodology for creating structural regimes with new magnetic properties, exploiting the spins of molecules for spintronic and quantum information-based device applications.

## References:

- [1] M. Warner *et al.*, *Nature* **503**, 504-508 (2013).
- [2] S. Heutz *et al.*, *Adv. Mater.* **19**, 3618-3622 (2007).
- [3] A. Follmer *et al.*, *J. Phys. Chem. A*, **124**, 9252–9260 (2020).
- [4] M. Atzori *et al.*, *J. Am. Chem. Soc.*, **138**(7), 2154-2157 (2016).
- [5] Z. Wu *et al.*, *Adv. Funct. Mater.*, **29**, 1902550 (2019).

**Effects of hydrophobic modification and electrostatic interactions on sensitivity of riboflavin-ascorbic acid radical pairs to weak magnetic fields**

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Photochemical reactions generate radical pairs that are spin correlated. Coherences between quantum mechanical states can persist long enough for weak magnetic interactions to have significant influence on the spin dynamics, and consequently, the reaction rates and product yields of the radical pair. This quantum mechanical phenomenon could be leveraged to develop new devices for navigation and global positioning. One requirement for a radical-pair compass is enhanced sensitivity to weak (50-100  $\mu\text{T}$ ) fields. Some flavin-based radical pairs exhibit this enhanced sensitivity when incorporated into a micelles environment. In order to leverage this effect in the development of novel magnetosensitive materials, we have undertaken systematic investigations of a series of ascorbic acid donors and flavin acceptor incorporated into ionic micelles. Magnetic field effects were characterized by prompt-fluorescence detection magnetically altered reaction yield measurements. Interpretation of these results is complimented by characterization of micellar properties and fluorescence quenching experiments to more fully understand the location and diffusional dynamics of the donor and acceptor molecules. By varying the charge of the micelle and employing chemical modification of the donor and acceptor, we demonstrate the utility of combining hydrophobic and electrostatic effects to maximize sensitivity of flavin radicals to weak magnetic fields.

## **What comes after the radical pair mechanism? - Understanding the protein conformational changes that allow avian navigation**

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It is hypothesised that the putative magnetoreceptor protein cryptochrome enables night-migratory birds to navigate using the Earth's magnetic field[1]. Following a well-established radical pair mechanism[2], different downstream chemical and biochemical reactions are thought to take place depending on how the inclination of the Earth's magnetic field influences the singlet and triplet yields of the magnetically sensitive radical pair[3]. This is thought to lead to protein conformational changes followed by protein-protein interactions with interaction partners[4].

We have investigated these conformational changes and interactions as the first steps of the magnetoreception signalling process using native mass spectrometry, mass photometry, chemical crosslinking followed by mass spectrometric analysis, and hydrogen-deuterium exchange mass spectrometry (HDX-MS). The latter technique is capable of discovering interaction surfaces and conformational changes by comparing surface exposures. Recently, we were able to see conformational changes in certain protein regions of cryptochrome 4 of several bird species using this method. Differences were seen when the experiments were performed with and without blue light. Furthermore, a static applied magnetic field seems to have an impact on the magnitude of these differences.

By mapping conformational changes found in molecular dynamics simulations onto the changes observed using HDX-MS, we hope to fill the gaps left by the current experimental data.

As dimers of non-bird species seem to play important roles in nature[5], we used chemical crosslinking to narrow down the interaction surface between monomers in potentially functional dimeric cryptochrome structures complemented by molecular dynamics simulations. To further investigate the interaction surface, we recently also started looking into using electron paramagnetic resonance spectroscopy to complement the data acquired so far.

Using a range of complementary techniques, we hope to elucidate protein conformational changes in several bird cryptochromes, answer the question whether a functional dimer might exist in the context of magnetoreception and investigate the interaction surfaces in these dimeric structures and between cryptochrome and its interaction partners.

Acknowledgements. We are grateful to Jessica Schmidt, Rabea Bartölke, Jingjing Xu, and Shambhavi R. Apte for samples of the cryptochromes studied here.

[1] T. Ritz *et al.*, *Biophys. J.* **78**, 2 (2000)

[2] J. Xu *et al.*, *Nature* **594**, 7864 (2021)

[3] P. J. Hore *et al.*, *Annu. Rev. Biophys.*, **45** (2016)

[4] H. Wu *et al.*, *Sci. Rep.* **10**, 1 (2020)

[5] K. Shao *et al.*, *Nat. Struct. Mol. Biol.* **27**, 5 (2020)

# The influence of dynamical degrees of freedom on compass sensitivity: A comparison of plant and migratory bird cryptochromes

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The magnetic compass of migratory birds is thought to rely on the radical pair mechanism operating inside a cryptochrome blue-light photoreceptor [1]. It is imperative that the radical pair exists in a nonequilibrium coherent state long enough for the Earth's magnetic field to have an influence on the underlying coherent spin dynamics. Fluctuations of pertinent interactions weaken the coherence of the radical pair in a process called spin relaxation [2]. Here, we investigate the dynamical properties of relevant dihedral and librational angles in the flavin adenine dinucleotide ( $\text{FAD}^{\cdot-}$ ) and tryptophan ( $\text{Trp}^{\cdot+}$ ) radical pair inside cryptochrome 4a from European robin (*ErCry4a*) and cryptochrome 1 from *Arabidopsis thaliana* (*AtCry1*) to characterise the implications of thermal motion on compass sensitivity. This analysis relies on the time-dependent hyperfine interactions in the  $\text{FAD}^{\cdot-}$  and  $\text{Trp}^{\cdot+}$  radicals, which permit calculation of the quantum yield anisotropy of the radical pair recombination influenced by an external magnetic field. The quantum yield anisotropy is a measure for the sensitivity of the birds' magnetic compass. The quantum yield anisotropy and dynamical parameters were compared for radical pairs in *ErCry4a* and *AtCry1* to determine whether evolutionary optimization of motional degrees of freedom in the avian radical pair could lead to a significantly better detection of the magnetic field.

## References

- [1] J. Xu et al., *Nature*, **594**(7864), 535–540 (2021)
- [2] D. Kattnig et al., *Phys. Chem. Chem. Phys.* **18**, 12443–12456 (2016)

## Detection of Magnetic Field Effects in Cryptochrome Proteins using Confocal Microscopy

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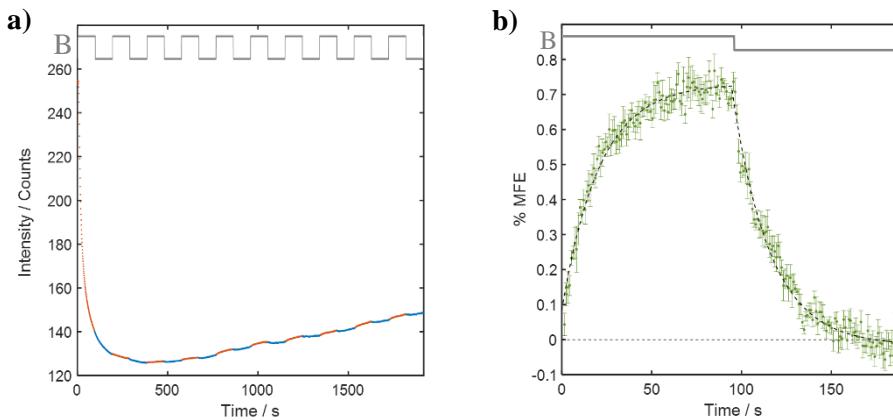
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Magnetic field effects (MFEs) on the yields and kinetics of chemical reactions are well-established and are thought to underlie the ability of migratory birds to navigate with high precision during seasonal migration, using the geomagnetic field [1]. This hypothesis is based on the generation of a radical pair within a blue-light photoreceptor protein, cryptochrome (Cry), which is found in the bird's retina [2]. Substantial differences in the *in-vitro* MFEs of Cry4 wild type (WT) proteins, sourced from the European robin (*Erithacus rubecula*), a migratory songbird, and a non-migratory chicken (*Gallus gallus*) have recently been reported [3].

Two residues, which are highly conserved in the Cry4 proteins of night migratory songbirds (e.g. *ErCry4* WT), but absent in *GgCry4* WT, could, in part, account for the observations in [3]. In order to test this hypothesis, a confocal fluorescence microscopy apparatus has been adapted for MFE detection [4]. In this work, MFEs in *GgCry4* WT (Fig. 1) are contrasted with those of single-point mutants, *GgCry4* R317C and *GgCry4* E320K, in which two highly conserved residues from *ErCry4* WT are substituted into *GgCry4* WT. The effect of these mutations on the MFE is then compared to the impact of shortening the electron transfer chain, responsible for radical pair formation, using a further single-point mutant, *GgCry4* W369F.



**Fig 1:** **a)** Time evolution of the fluorescence of *GgCry4* WT, photoexcited continuously from  $t = 0$ . The magnetic field (B, shown in grey) is switched between 0 mT (blue fluorescence segments) and 17 mT (red fluorescence segments) producing a biphasic modulation in the fluorescence intensity. **b)** Time-averaged %MFE of *GgCry4* WT. The background variation of the fluorescence in **a**) is fitted and subtracted from the data, and the obtained background-subtracted signal is averaged over all field-cycles to yield the mean %MFE. As before, the magnetic field is shown in grey.

- [1] P. J. Hore, H. Mouritsen, *Annu. Rev. Biophys.*, **45**, 299-344 (2016)
- [2] T. Ritz *et al.*, *Biophys. J.*, **78**, 707-718 (2000)
- [3] J. Xu *et al.*, *Nature*, **594**, 535-540 (2021)
- [4] V. Déjean *et al.*, *Chem. Sci.*, **11**, 7772-7781 (2020)



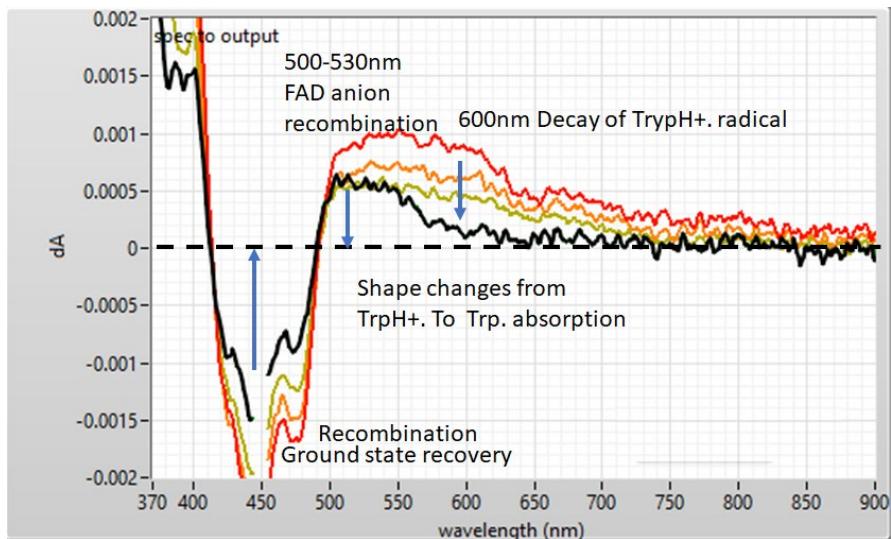
## Magnetic Field Effects in Avian Cryptochrome Proteins

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The magneto-sensitive radical recombination reactions in avian cryptochrome proteins have been demonstrated using a variety of photochemical methods [1]. A complete understanding of the mechanism is yet to be established and a topical discussion ensues on how these processes might explain migratory behaviour in biological systems. It is a startling and surprising fact that deep inside the avian cryptochrome proteins lies a spatially separated, spin correlated radical pair that shows a significant magneto-sensitive response. The magnetic field sensitivity is dependent on the specific location along a pathway of tetrad of tryptophan residues with optimised geometry and orientational configuration. In this poster, we describe picosecond transient absorption experiments revealing the effect of a single site substitution of the different tryptophan's and neighbouring amino acids on the magnitude of the MFEs for (Chicken) GgCry4 cryptochromes. The kinetic and magnetic sensitive properties of GgCry4WT proteins and modified GgCry4 proteins are compared and discussed with results found for (Robin) ErCry4W369F and (Quail) CcCry4W369F proteins.

### Reference

[1] Xu Jingjing et al., *Nature*. 23<sup>rd</sup> June, (2021).





## Electron spin delocalization in radical anions of porphyrin molecular wires

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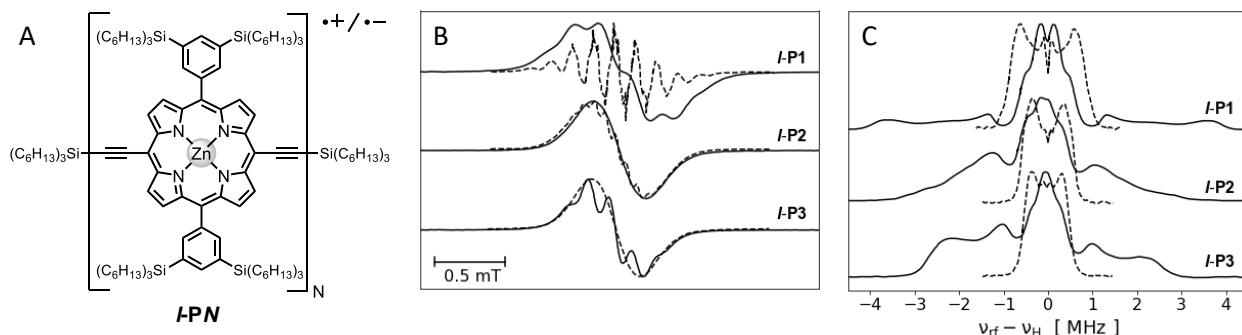
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Chains of butadiyne-linked porphyrins (Figure 1 A) have been shown to function as molecular wires, making them interesting for applications in spintronics and photovoltaic devices. [1] Porphyrins are attractive building blocks for molecular electronics as they facilitate efficient charge transport and their electronic properties can be synthetically fine-tuned. Charge-doping of porphyrin oligomers with holes or electrons can be used to enhance the communication between adjacent porphyrins, and previous work demonstrated delocalization over 2–3 porphyrin units in porphyrin radical cations. [2]

In this work we investigate the extent of electron spin delocalization in chemically reduced butadiyne-linked porphyrin chains. We compare our results to the previously reported oxidized systems to find out if n- or p-doping results in more efficient delocalization and therefore which is more suitable for charge transport applications. X-band CW-EPR (Figure 1 B), pulsed EPR measurements at Q- and W-band and ENDOR spectroscopy (Figure 1 C) were used to study the delocalization and mobility of polarons. There is a noticeably different spin density distribution in radical cations and anions: while spin density is largely located at the inner porphyrin nitrogen atoms in the cations, more spin density is distributed over the outer ring of the porphyrin  $\pi$ -system in the anions, resulting in larger proton hyperfine couplings. Interpretation of the experimental data was aided by DFT calculations and simulations.

Our measurements indicate more efficient delocalization in the radical anions of porphyrin oligomers compared to the cations. These results contribute to our understanding of polaron delocalization and are expected to guide future designs of molecular wires.



**Figure 1:** (A) Structure of porphyrin oligomers **I-PN**. (B) CW-EPR spectra (294 K) and (C)  $^1\text{H}$  Mims ENDOR spectra (80 K) of I-PN anions (solid lines) and cations (dashed lines). Data for I-PN cations was adapted from [2].

[1] G. Sedghi, et al., *Nat. Nanotech.* **6**, 517-523 (2011)

[2] M. D. Peeks, C. E. Tait, et al., *J. Am. Chem. Soc.* **139**, 10461-10471 (2017)



# Limits of Nuclear Spin Singlet Lifetimes from Experiment and Molecular Dynamics Simulations

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Magnetization encoded in nuclear spin singlet states have been shown to exhibit lifetimes exceeding spin-lattice relaxation times several fold, with impressive demonstrations of singlet lifetimes of more than an hour in organic molecules in solution. Such long lifetimes have inspired the search for applications including measurements of slow dynamic processes, the development of MRI contrast agents, and even the search for nuclear spin state roles in quantum biology and quantum cognition.

The underlying lifetime limits of singlet order are often difficult to pinpoint. Over the years, several relaxation mechanisms have been identified, including dipolar coupling, chemical shift anisotropy, paramagnetic relaxation, spin rotation and spin-internal motion, and the scalar relaxation of the second kind. While in principle, many of the mechanisms are well understood, estimating their size can be difficult. Furthermore, multiple experimental examples have been found that decidedly defy expectations.

We present here work on directly estimating singlet relaxation mechanisms by experimental isolation and comparing with molecular dynamics simulations. Here we show calculations for intermolecular mechanisms and find good agreement with experiment [1]. It is particularly surprising to see that such mechanisms as intermolecular coupling to  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclear spins (of the chloroform solvent) could be rate limiting for singlet states in a particular model system (Fig. 1).

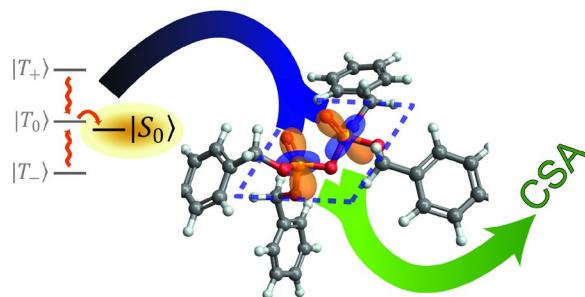


Fig. 2: Visualization of CSA tensors responsible for CSA relaxation in phosphate-based  $^{31}\text{P}$  singlets.

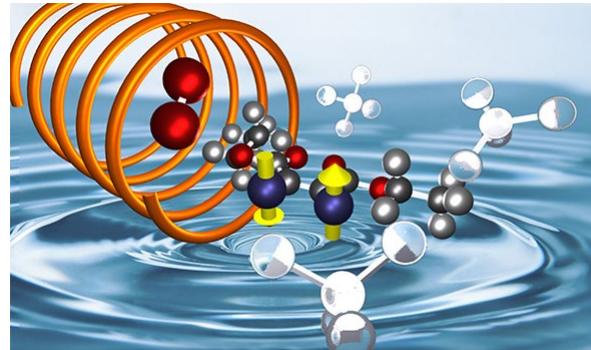


Fig. 1: Ethyl-propyl dimethyl maleate, together with chloroform and oxygen, the main actors in the processes investigated.

In addition, we also show work on  $^{31}\text{P}$  spin singlets, and compare their lifetimes to those from molecular dynamics trajectories and ab initio calculations of chemical shift anisotropy (CSA) tensors (Fig. 2), which show good agreement. Calculations of this sort may help in the design of particularly long-lived singlet states, or could be used to identify new probes for dynamics.

**References should be listed as below**  
[1] B. Kharkov *et al.*, *Phys Chem Chem Phys*. **24**, 7531 (2022)

## Fluorescence-based magnetic field effects on a protein-flavin complex

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The interest in protein-ligand interactions is of great importance to the field drug delivery and cancer research [1]. Recently, magnetic field effects (MFEs) have provided novel insights into protein-ligand dynamics [2]. Here, we present a new approach for investigating protein-ligand binding dynamics in the form of magnetically sensitive single photon microspectroscopy. Recent work on bovine serum albumin (BSA) and anthraquinone-2,6-disulfonate (AQDS) observed long-lived radical pairs and large magnetic field effects [3]. Due to the surge in interest in the flavoprotein cryptochrome radical pair hypothesis, we aimed to develop a BSA-flavin model.

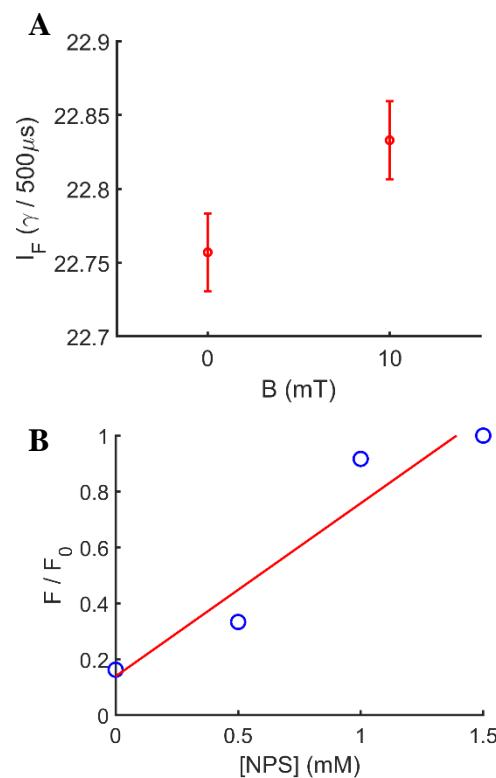
Fig. 1A displays an MFE on the BSA-FMN complex. The sign of the MFE is positive, which suggests a singlet born radical pair (which are also observed in the cryptochrome protein). The FMN binding position within the protein was investigated with molecular docking simulations and competitive binding experiments. The known crystal structure of the BSA-naproxen (NPS) complex [4] and docking results were combined to elucidate the FMN binding site. Fig. 1B exhibits FMN fluorescence recovery with increasing NPS concentration. Results suggest that FMN is located *ca.* 4 Å away from W211 inside the BSA binding pocket, supporting the observed singlet born magnetic field effect. Further experimental observations will be presented and discussed.

### References

- [1] D. Mattanovich *et al.*, *Microbial Cell Factories* **5** (1) (2006)
- [2] T. Miura *et al.*, *J. Phys. Chem. B*, **107**, 6474-648 (2003)
- [3] N. Iwata *et al.*, *Submitted for publication*
- [4] F. Bou-Abdallah *et al.*, *J. Chem. Thermo.* **103**, 299-309 (2016)

### Acknowledgements

Supported by JST PRESTO (Quantum Bio) Grant No. JPMJPR19G1



**Figure 1:** **A.** Single-photon avalanche diode detected MFE on BSA (0.5 mM)-FMN (200 nM) in water. **B.** Competitive binding experiment with BSA (0.5 mM)-FMN (200 nM) and NPS.



## Pulsed and Continuous-Wave, Solid-State, Room-Temperature Masers

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One of the main current uses of masers is for deep space communication, due to their ability to function as extremely low noise amplifiers. However, most masers work under inconvenient conditions, such as low temperatures that require liquid helium for cooling. In this talk, I will discuss our project to build a continuous-wave, solid-state maser based on molecular triplet states and working at room temperature.

Initial experiments used the photo-excited triplet state of pentacene doped into a *p*-terphenyl single crystal. Anisotropic intersystem crossing to the lowest triplet state with its associated zero-field splitting following pulsed laser excitation creates a population inversion in a pseudo two level system at zero magnetic field. A dielectric ( $\text{SrTiO}_3$ ) resonator with a high Purcell factor was designed to enhance the stimulated emission and thus pulsed maser operation was achieved at 1.45 GHz. The kinetics could be modeled using a pair of first-order nonlinear differential equations, often referred to as the Lotka–Volterra or predator–prey equations due to their use in modeling population dynamics in biology [1]. Furthermore, we observed Rabi oscillations in the microwave emission of samples containing a large number of pentacene molecules. This indicates that we have reached a regime in which the spin ensemble and the photons in the microwave resonator mode are strongly coupled. We also observed a cavity protection effect at the onset of the strong-coupling regime that decreases the polariton decay rate as the collective coupling increases [2].

However, a continuous-wave maser is needed for technological applications. We recently achieved this at room temperature by employing NV- centres in diamond which have a triplet ( $S = 1$ ) ground state ( $D \sim 2.87$  GHz), a 532 nm laser to polarize the electron spins, a dielectric (sapphire) resonator ( $v \sim 9.2$  GHz) to enhance the stimulated emission and an external magnetic field to tune the resonance via the Zeeman interaction [3].

## References

- [1] E. Salvadori *et al.*, Scientific Reports 7, 41836 (2017)
- [2] J.D. Breeze *et al.*, npj Quantum Information 3, 40 (2017)
- [3] J.D. Breeze *et al.*, Nature 555, 493-496 (2018)

Title: Determination of  $^{13}\text{C}$  CSA tensor of selective labelled on photosynthetic heliobacterial reaction center by solid-state photo-CIDNP MAS NMR SUPER experiment

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Solid-state photo-CIDNP MAS NMR is a powerful analytical tool to investigate natural photosynthetic reaction centers (RCs). In the heart of the RCs, the electron transfer is initiated by the excitation of the electron donor pair, which donates an electron to an acceptor forming a spin-correlated radical pair (SCRP) [1]. The spin-evaluation of the SCRP is accompanied by the solid-state photo-CIDNP effect which can be detected by solid-state NMR with the strong signal enhancement at electron donor and acceptor cofactors.

The heliobacterial RC is proposed to be an evolutionary ancient of extant RCs since it has the simplest homodimeric structure known [2]. Previously, we observed that the solid-state photo-CIDNP effect on heliobacterial RC is strongly magnetic field dependent indicating different mechanisms of contributing to the effect [3]. The light induced absorptive signals originated from BChlg as the electron donor are dominant at 4.7 T whereas emissive signals originated from Chla $F$  as the electron acceptor are predominantly observed at 9.7 T. In the present study, we determined the  $^{13}\text{C}$  CSA (chemical shift anisotropy) of both BChlg and Chla $F$  using selective [ $4\text{-}^{13}\text{C}$ ]-ALA labelling by modified SUPER (separation of undistorted powder patterns by effortless recoupling) [4,5] experiment removing CP (cross polarization) for photo-CIDNP MAS NMR under the illumination. And our experiment was measured at two different magnetic fields, 4.7 T selectively for BChlg and 9.4 T for Chla $F$ . The determined CSA is expected to provide the insight into electronic structure and local dynamics of electron donor and acceptor cofactor.

- [1] J. Matysik et al., Photosynth. Res. 102 (2009) 427
- [2] G. S. Orf et al., Photosynth. Res. 138 (2018) 11
- [3] S. S. Thamarath et al., Biochemistry, 51 (2012) 5763
- [4] S-F. Liu et al., J. Magn. Reson. 155 (2002) 15
- [5] D. Gräsing et al., Sci. Rep. 9 (2019) 10528

## Influence of photodegradation on magnetic field sensitive protein-ligand photochemistry

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Microscopy is a powerful tool for elucidating biological processes within cellular environments. A major hindrance and concern when irradiating inherent cellular fluorophores is photodegradation. Flavins are biologically important molecules and are essential as active groups in flavoproteins in processes such as redox homeostasis and DNA repair [1]. The biological active group flavin mononucleotide (FMN) is known to photodegrade. Upon absorption of UV/blue light, the isoalloxazine ring experiences intramolecular photoreduction from the electron donor ribityl sidechain. Fragmentation may occur, during sidechain oxidation, to yield several photoproducts. FMN photodegrades predominately into lumiflavin (LF, 42 %) and lumichrome (LC, 58 %) [2].

To reduce photodegradation, low laser power and sample flow were used. To further understand the effect of photodegradation on biological samples, we measured fluorescence intensity and magnetic field effect (MFE) flow rate dependence, with single photon avalanche diode (SPAD) detection, on FMN in the presence and absence of the protein HEWL [3].

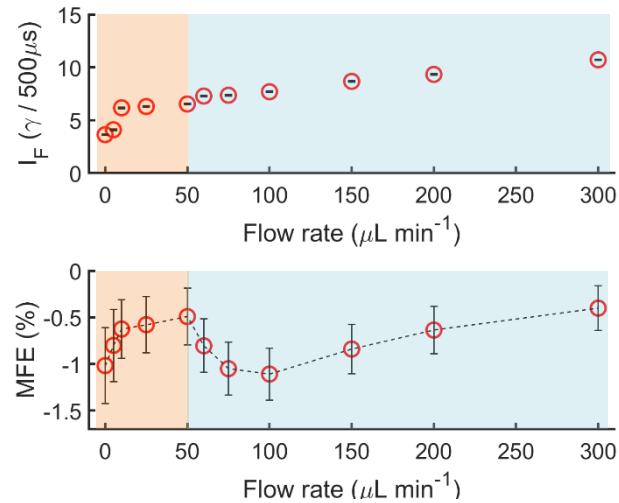
The fluorescence intensity and MFE magnitude changed significantly either side of the  $50 \mu\text{L min}^{-1}$  boundary, where the ratio of  $\text{LF} > \text{FMN}$  below the boundary and  $\text{FMN} > \text{LF}$  above the boundary (LC does not absorb at our excitation wavelength). This change can be attributed to the coulomb interaction between the ligand and protein surface, which disappears when FMN photodegrades to LF. The details of the experimental results and theoretical simulations will be presented and discussed.

### References

- [1] P. MacHeroux *et al.*, *FEBS Journal*, **278**, 2625-2634 (2011)
- [2] W. Holzer *et al.*, *Chem. Phys.*, **308**, 69–78 (2005).
- [3] T. Miura *et al.*, *J. Phys. Chem. B*, **107**, 6474-6478 (2003).

### Acknowledgements

Supported by JST PRESTO (Quantum Bio) Grant No. JPMJPR19G1



**Figure 1:** Single photon avalanche diode (SPAD) detection. Flow rate dependence on FMN (200 nM) + HEWL (0.5 mM) fluorescence intensities (top) and magnetic field effects (bottom) between 500-600 nm. 450 nm excitation (290  $\mu\text{W}$ ).



## Investigation of the Polaron Delocalization in Edge-Fused Porphyrin Oligomers by EPR and Optical Spectroscopy

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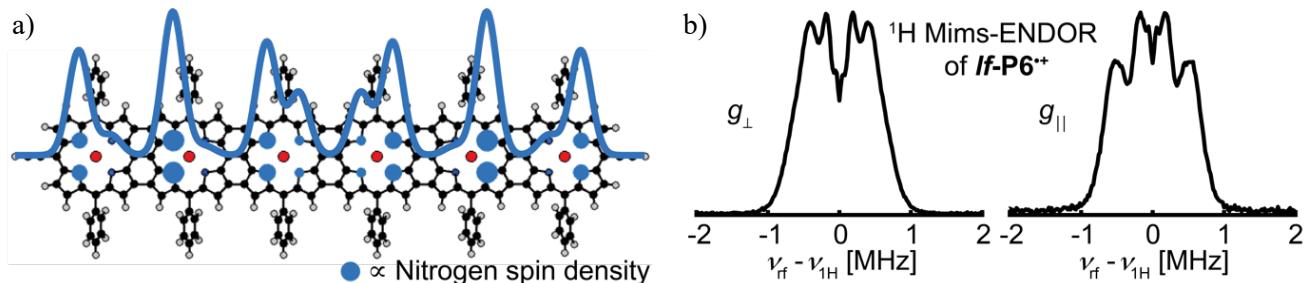
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The rational design, synthesis, and study of functional  $\pi$ -conjugated molecules with precisely tailored electronic properties is an intriguing approach toward the miniaturization of electronic circuits to the molecular level. Edge-fused porphyrin tape oligomers are particularly promising molecular wires because their HOMO-LUMO gaps decrease steeply with increasing chain length.<sup>[1]</sup>

In this work, we investigate the distribution of unpaired electrons along the molecular backbone of a series of porphyrin tape oligomer radical cations. These polarons are the principal charge carriers in organic wires, and it is essential to generate radicals with low electron-phonon coupling and long-range delocalization to achieve high molecular conductance.<sup>[2]</sup> We use a combination of continuous wave EPR, W-band  $^1\text{H}$  and  $^{14}\text{N}$  Mims-ENDOR spectroscopy, and supporting calculations to investigate the electronic structure of a series of porphyrin tape radical cations with  $n = 1-4, 6$ , and  $10$  porphyrin units in frozen and room temperature solutions (Figure 1). In addition, we used optical Vis-NIR-MIR spectroelectrochemistry to complement our EPR interpretation with solution state measurements on a faster time scale. The results demonstrate efficient polaron delocalization over up to at least ten porphyrin units ( $\sim 8.3$  nm) despite a substantial deviation from Norris trend<sup>[3]</sup> in their room temperature cw-EPR spectra and a discontinuous trend in the spectral envelopes of the  $^1\text{H}$  ENDOR spectra. For  $n \geq 6$ , we highlight the emergence of persistent radical cations under ambient conditions that increasingly dominate the electronic properties of the porphyrin tapes. These results are expected to inform the design of new efficient molecular wires.



**Figure 1.** a) Schematic structure of the porphyrin tape hexamer cation **If-P6<sup>+</sup>**. The superimposed DFT calculated  $^{14}\text{N}$  spin densities support a full delocalization of the polaron that results in an inhomogeneous spin density distribution along the molecule. b) W-band  $^1\text{H}$  Mims-ENDOR spectra of **If-P6<sup>+</sup>** with modest orientation selection for the two principal  $g$ -orientations.

- [1] A. Tsuda *et al.*, *Science* **79**, 293 (2001)
- [2] G. Moise *et al.*, *J. Phys. Chem. Lett.* **10**, 5708 (2019); M. D. Peeks *et al.*, *J. Am. Chem. Soc.* **139**, 10461 (2017)
- [3] J. N. Norris *et al.*, *Proc. Nat. Acad. Sci.* **68**, 625 (1971)



## **<sup>13</sup>C solid-state photo-CIDNP on a flavoprotein embedded in glassy sugar matrix**

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Phototropin is a blue light receptor containing flavin mononucleotide (FMN) in its LOV domain. After photoexcitation with blue light, the FMN forms a photoexcited triplet state which in natural occurring LOV domains reacts with a conserved nearby cysteine to form a covalent adduct. By mutation of the cysteine to a serine, the adduct formation is prohibited and the lifetime of the photoexcited <sup>3</sup>FMN is elongated. This induces a one-electron transfer from a tryptophan of the protein matrix (1 nm edge-to-edge distance) which in turn forms a radical pair as an intermediate leading to photochemically induced dynamic nuclear polarization (photo-CIDNP) signal enhancement in NMR which is observable in both solid and liquid states [1]. Here, isotope enrichment of <sup>13</sup>C and <sup>15</sup>N allows the selective detection of the hyperpolarized signals from both partners involved in the electron transfer.

The measurement time under illumination, however, is limited because of the generation of singlet oxygen by the photoexcited <sup>3</sup>FMN [2] which enhances the photodegradation of the protein. Besides, expensive and not straightforward isotope labelling can prohibit the search for photo-CIDNP in newly discovered proteins and impede further investigations on known ones. Therefore, an increase in stability of the protein under illumination can enable the use of two-dimensional solid-state photo-CIDNP NMR techniques for further investigations.

Here, we present an approach where the protein is embedded into a sugar glass matrix and measured with <sup>13</sup>C solid-state photo-CIDNP NMR. This has the advantage that the solid-state experiment can be performed at room temperature while simultaneously prolonging the measurement time to investigate unlabeled protein samples here presented for LOV1 of phototropin C57S.

### **References**

- [1] Y. Ding et al, Sci. Rep., **9**, 184436 (2019).
- [2] M. Petrencakova et al, Sci. Rep., **10**, 4119 (2020).

# Persistent Radicals in Irradiated Imidazolium Ionic Liquids Probed by EPR Spectroscopy

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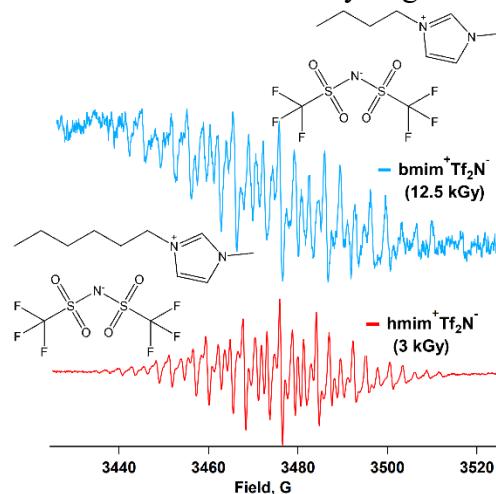
We probe the radiation stability of imidazolium RTILs relevant to their use in nuclear waste separation using cw-EPR spectroscopy. Long-lived radicals were observed in irradiated room temperature ionic liquids (RTILs) composed of the bis(trifluoromethylsulfonyl)imide anion ( $\text{Tf}_2\text{N}^-$ ) with 1-hexyl-3-methylimidazolium ( $\text{hmim}^+$ ) and 1-butyl-3-methylimidazolium ( $\text{bmim}^+$ ) cations. The EPR signal intensity increases within hours and the spectral pattern changes during the time after irradiation. We demonstrated that oxygen does not react rapidly with these persistent radical species formed which indicates the absence of carbon-centered radicals. The kinetics data obtained indicate the existence of two radical species that have different formation and decay rates. Careful fitting of the spectrum data showed that the first radical contains 12 hydrogens with a splitting of 8 Gauss and 2 hydrogens with a splitting of 2.8 Gauss.

We applied the isotope deuteration effect to suggest possible structures of the stable radicals formed. Based on the data on the radicals formed in irradiated deuterated  $\text{bmim}^+\text{Tf}_2\text{N}^-$ , it was found that splittings of 8 Gauss come from methyl groups at nitrogen atoms, and hydrogen atoms with 2.8 Gauss come from C4 and C5 positions of the imidazole ring.

Extensive computational quantum chemistry calculations were performed to attempt to identify the structure of these persistent radicals generated by radiolysis of imidazolium RTILs.

On the basis of both experimental and calculated data, it can be concluded that the spectrum consists of cation radicals which have different kinetics. The structure of the first radical cation contains 12 hydrogens with an 8 Gauss splitting and 2 hydrogens with 2.8 Gauss. The structure of the second radical is characterized by a smaller number of hydrogens with 8 Gauss, which may indicate the dehydrogenation of the first radical. Unfortunately we have been unable to identify the exact structure of the resulting radicals since the structure contains a signal of a large number of hydrogen atoms, which is difficult to interpret as an imidazole derivative.

The obtained results should be considered when assessing the radiation stability of imidazole ionic liquids, which were proposed as potential solvents for the extraction of spent nuclear fuel and other energy-related applications.



**Fig.1** Comparison of EPR spectra obtained after radiolysis of  $\text{bmim}^+\text{Tf}_2\text{N}^-$  (12.5 kGy, blue) and  $\text{hmim}^+\text{Tf}_2\text{N}^-$  (3 kGy, red).

On the basis of both experimental and calculated data, it can be concluded that the spectrum consists of cation radicals which have different kinetics. The structure of the first radical cation contains 12 hydrogens with an 8 Gauss splitting and 2 hydrogens with 2.8 Gauss. The structure of the second radical is characterized by a smaller number of hydrogens with 8 Gauss, which may indicate the dehydrogenation of the first radical. Unfortunately we have been unable to identify the exact structure of the resulting radicals since the structure contains a signal of a large number of hydrogen atoms, which is difficult to interpret as an imidazole derivative.

## Structure and kinetics of organic radicals from EPR

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We apply continuous-flow EPR spectroscopic techniques to detect both spectra and kinetics of organic radicals in solution at room temperature. We are investigating this EPR method to evaluate the radiation chemistry and stability of organic ligands used in the solvent extraction processes for nuclear waste separation [1-2]. In the process of such waste separations, unavoidable radiolysis of both the aqueous and organic phases generates a wide variety of more or less transient radicals.

While overall molecular degradation can be determined using standard product analysis techniques, EPR spectroscopy can be used to unambiguously identify the short-lived precursor organic radical intermediates formed in such separation solutions.

In recent work [3], we have shown the possibility of employing this technique to successfully identify both structures and kinetics of such organic radicals. Chemical methods (such as the Fenton system) will be used to generate inorganic and organic radicals in the EPR cavity. The incoming reagent streams are mixed rapidly prior to entry into the EPR cavity for detection. Due to the fast flow following mixing, a steady-state concentration of radicals is quickly established. EPR spectra can be recorded at various solution flow rates to allow elucidation of the reaction kinetics. We will also explore the possibility of applying photochemical methods (UV-light/H<sub>2</sub>O<sub>2</sub>) to generate radicals directly.

Various radicals derived from organic ligand complexes in aqueous solution will also be examined using rapid-flow EPR experiments employing a mixing resonator, again at room temperature.

Complementary to these experimental approaches, detailed quantum chemical calculations will be conducted on a number of potential radicals derived from such molecular species and ligands. First, geometries of the candidate radicals will be optimized using Density Functional Theory techniques in the presence of a surrounding solvation field. Hyperfine coupling constants will be determined at these optimized geometries from single-point calculations using the B3LYP functional, with a basis sets specifically designed to accurately recover the required nuclear spin densities. The effects of intramolecular vibrations on the calculated coupling constants will be assessed by vibrational perturbation theory.

### References

- [1] J. Veliscek-Carolan, *J. Hazard Mater.* **318**, 266-281, (2016)
- [2] P. Baron et al., *Progress in Nuclear Energy*, **117**, 103091 (2019)
- [3] A. Lisovskaya, O. Shadyro, O. Schiemann, I. Carmichael, *PCCP*, **23** (2), 1639 (2021)

## **Interaction of a photogenerated spin qubit pair with a stable radical in DNA hairpins**

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Tunable molecular systems that can generate entangled electrons, or spin qubit pairs (SQPs), are highly desirable for developments in quantum information science (QIS). Photogenerated SQPs can be initialized in a pure quantum state which exhibits relatively long coherence times, allowing for electron spin manipulation via optical and magnetic spectroscopy. DNA hairpins serve as a modifiable scaffold on which to study these multi-spin interactions, such as a SQP in conjunction with a stable radical. Such a multi-spin system is optimal for implementing spin manipulations that could be advantageous for executing quantum logic gates and spin teleportation. DNA hairpins also offer the possibility of individual qubit addressability and qubit scalability. Here, we examine a series of DNA hairpins that use naphthalenediimide (NDI) as the hairpin linker and chromophore, and guanine or an organic endcap as the terminal hole acceptor. A stable nitroxide radical is covalently attached to the hairpin to facilitate spin interactions between the SQP and stable radical. Electron paramagnetic resonance spectroscopy and ultrafast optical spectroscopy are utilized to explore the charge transfer rates and spin-spin interactions in these DNA hairpins to determine how the SQP pair interacts with the stable nitroxide radical, and how this modulates the overall dynamics of the system.

## **Relaxation-induced time-dependence of $B_{1/2}$**

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The  $B_{1/2}$  value is the magnetic field that produces 50% of the limiting (high-field) change in the product yield of a radical pair reaction. It is used to characterize the sensitivity of the reaction to the strength of the field.  $B_{1/2}$  is often calculated using the Weller equation [1] and is not generally considered be time-dependent. However, recent experiments [2, 3] have consistently observed time-dependent  $B_{1/2}$  values. We consider that this originates in a specific relaxation mechanism, which was ignored in [1], but was discussed at some detail in [4]. Therefore, we tested several possible relaxation mechanisms for radical pairs in cryptochromes by means of spin dynamics simulations to find those that could lead to a time-dependent  $B_{1/2}$ . We find that singlet-triplet dephasing (STD) is the most probable mechanism to account for this phenomenon. Furthermore, we find theoretical evidence for the long-term modulation of the reaction product yields as a result of STD. We were able to fit the time-dependent magnetically altered reaction yield (MARY) data of the TrpD mutant of *ErCry* (*Er*, *Eriothacus rubecula*) of the European robin and *DmCry* (*Dm*, *Drosophila melanogaster*) of the fruit fly, using a semi-classical method [4] with STD included.

### **References**

- [1] A. Weller *et al.*, *Chem. Phys. Lett.* **96**, 24-27 (1983)
- [2] T. Zollitsch, PhD thesis, University of Oxford (2018)
- [3] M. Golesworthy, PhD thesis, University of Oxford (2021)
- [4] K. Maeda *et al.*, *Mol. Phys.* **104**, 1779 (2006)

## Design guidelines for optimising triplet formation in PDI–radical systems

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Owing to the tunability of their optical and magnetic properties, organic molecules are ideal candidates to study spin–spin interactions and how to manipulate them.<sup>[1]</sup> A deeper understanding of spin communication will be crucial for identifying novel materials for applications in molecular spintronics. Perylene diimides (PDIs) are a class of molecules that exhibit the required chemical and optical properties to be employed as building blocks for such applications. When linking the PDI to a stable radical, such as TEMPO or trityl, the triplet state of the PDI can be generated after photoexcitation by 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.<sup>[2]</sup> Here, we use optical

spectroscopic techniques, such as femtosecond UV-vis transient absorption and transient electron paramagnetic resonance spectroscopies, to investigate the interactions between the building blocks of a series of modified PDI–radical systems. We determine the influence of PDI core substituents on the systems' optical and magnetic properties, as well as the influence of introducing a second radical substituent in the imide position of the PDI on the kinetics and yields of the competing excited state processes. Our results show the generation of quartet or quintet states after photoexcitation of the PDI moieties, indicating strong coupling between the chromophore triplet and the nitroxide radical(s). The fastest EISC rate constant is observed for a PDI without core substituents. However, in contrast to expectations, this did not lead to an increased triplet yield. Considering the yields of other excited state deactivation processes, competing with EISC, we are able to rationalise this observation, leading us to propose design guidelines for molecular systems comprising chromophores in which the higher excited states can be efficiently sensitised in proximity of an unpaired electron spin.

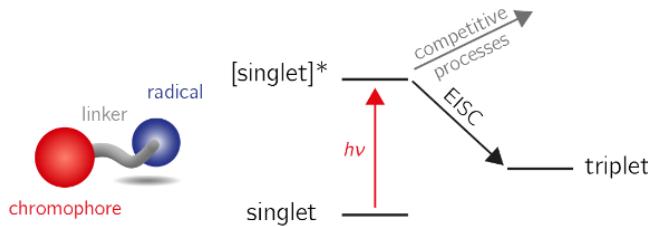


Figure 1: Through light excitation of the chromophore the excited singlet state is formed. Subsequently, the triplet state can be generated by enhanced intersystem crossing (EISC).

## References

- [1] S. Sanvito *Chem. Soc. Rev.* **40**, 3336 (2011)
- [2] M. Mayländer *et al.*, *J. Am. Chem. Soc.* **143**, 7050 (2021)

## The role of quenching and diffusion in tuning the magnetic sensitivity of micellar thionine-aniline radical pairs

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For many years, magnetic field effects (MFEs) in chemical systems have been under investigation owing to the fact this phenomenon is thought to be the origin of the avian compass sense. Known as the radical pair mechanism (RPM), this theory posits that weak magnetic field can influence the reaction rate or product yield of photochemical reactions by a process of coherent spin mixing between the singlet and triplet states of a spin-correlated radical pair. Photo-induced electron transfer occurring in micellar solutions have long been employed as model systems for MFEs developing through the RPM. We have undertaken a re-examination of a common model system: a thionine electron acceptor and aniline electron donor in micellar solutions of sodium dodecyl sulfate (SDS). Spectroscopic measurements of MFEs in this system with sub-nanosecond time resolution demonstrated an unexpected sign change that is both time and concentration dependent. The sign of a MFE arising from the RPM should correlate to the spin state of the excited state precursor to the radical pair. Intersystem crossing of thionine occurs on a picosecond timescale, while electron transfer leading to formation of the radicals has generally been considered slower; therefore, all previous reports of MFEs on thionine/aniline radical pairs have assumed to arise from a triplet precursor. Our unusual results regarding the sign of the MFE suggest two possible origins: previously unreported competition between static and dynamic quenching of micellized thionine/aniline leads to formation of both singlet-born and triplet-born radical pairs or the observed MFE arises from a different mechanism altogether. To investigate the origins of this effect, we have undertaken systematic investigation using NMR, optical spectroscopy, and fluorescence quenching to characterize the incorporation of thionine and aniline in the micelles as well as details of their interactions that may influence the observed magnetic field effects.

## Time-resolved EPR studies on two types of radical pairs in the BSA-AQDS complex under frozen conditions

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Serum albumin is one of the most abundant proteins found in blood. Serum albumin binds a variety of ligands and plays essential roles in their transportation, distribution, and metabolism [1]. Anthraquinone-2,6-disulfonate (AQDS) is one of the ligands of bovine serum albumin (BSA) which forms a radical pair via photo-induced electron transfer. Recently, a clear low field effect was observed in the BSA-AQDS system [2,3]. Since the hypothesis of a radical pair compass is known to be the primary candidate mechanism for magnetoreception in migratory birds, the BSA-AQDS complex is an interesting model for elucidating the processes which enable magnetoreception. However, the mechanism of the low field effect in the BSA-AQDS complex is still unclear and which amino acid residue reacts with the AQDS to form a radical pair is unknown. Thus, the structural and spin dynamical information of the BSA-AQDS complex is required to clarify the mechanisms attributing to the low field effect.

Time-resolved electron spin resonance (TREPR) spectroscopy is one of the most powerful tools to characterise radical pairs. We applied TREPR to the BSA-AQDS mixture, where the sample was degassed by freeze-pump-thaw cycling. TREPR measurements were carried out under frozen conditions using a Bruker E580 spectrometer and a CF935 cryostat temperature control system. The samples were excited by a Nd:YAG laser (355 nm, 13 mJ, 10 Hz). The TREPR spectra were analysed by the electron spin polarisation transfer model [4, 5].

Fig. 1 shows the TREPR spectra of the BSA-AQDS system with varying concentrations of BSA and AQDS. A broad TREPR signal was observed in the range of 320-360 mT for the [BSA]:[AQDS] ratio of 2:1. The EPR signals using a linearly polarised excitation laser exhibited anisotropy indicating that the position and orientation of the radical pair are fixed with respect to the transition dipole moment of the AQDS ligand within the protein. When the concentration of AQDS is higher than that of BSA, a narrow signal between 337-344 mT appears. The broad and narrow signals are attributed to proximal (~0.5 nm) and distal radical pairs, respectively. These findings suggest that at least two different radical pairs are generated in BSA-AQDS. Further analysis using Q-band TREPR, spectral simulations, and pulsed-EPR will be discussed.

- [1] Peters, T. *Adv. Protein Chem.*, 37, 161-245 (1985).
- [2] Iwata and Maeda, *Spin Chemistry Meeting* (2019)
- [3] Iwata *et al.*, submitted.
- [4] Kobori and Fuki, *JACS*, 133, 16770-16773 (2011).
- [5] Fuki *et al.*, *J. Phys. Chem. B*, 120, 4365-4372 (2016).

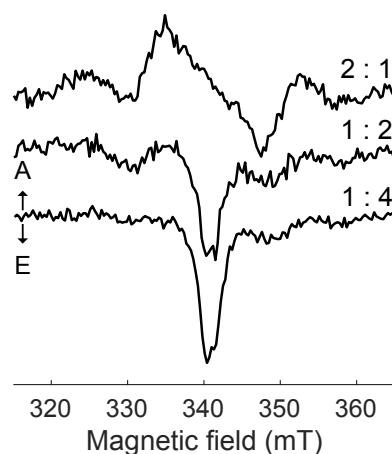


Fig 1. TREPR spectra of the BSA-AQDS at various concentration ratios.

# **Enhanced Quantum Cooling of Microwave Cavities Using the Photoexcited Triplet State of Pentacene Doped p-Terphenyl**

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The photoexcited triplet state of pentacene doped p-terphenyl (pc:ptp) has been shown to be capable of transiently cooling a microwave cavity to cryogenic noise temperatures through stimulated absorption of the thermal photon population [1]. This process occurs after an epoch of low noise maser amplification, which has shown significant promise in the field of quantum sensing [2]. Combined, these processes may enable the preparation of a microwave cavity in an ultralow-noise state, into which a signal could be injected and then maser amplified to produce a new type of quantum sensor. Importantly, due to the lack of complicated and expensive cooling apparatus, this system is a candidate for a commercially practical method of attaining ultrahigh sensitivity microwave detection, as is required in various current and emerging quantum technologies [3]. We here present the progress which has been made towards optimising the performance of both the masing and cooling regimes through invasive optical pumping of pc:ptp crystals grown onto Ce:YAG luminescent concentrators, resulting in improvements in masing duration and cooling performance. Further, we investigate the magnetic inversion of pentacene's triplet sublevels through the Zeeman effect, producing an absorptive-emissive transition which would offer improved utility compared to the emissive-absorptive transitions in pc:ptp at zero field.

## **References:**

- [1] Wu, H. et al. Physical Review Letters. 127 (5), 053604 (2021)
- [2] Wu, H, et al. arXiv preprint. arXiv:2201.04298. (2022)
- [3] Degen, C.L, et al. Reviews of Modern Physics. 89, 035002 (2017)

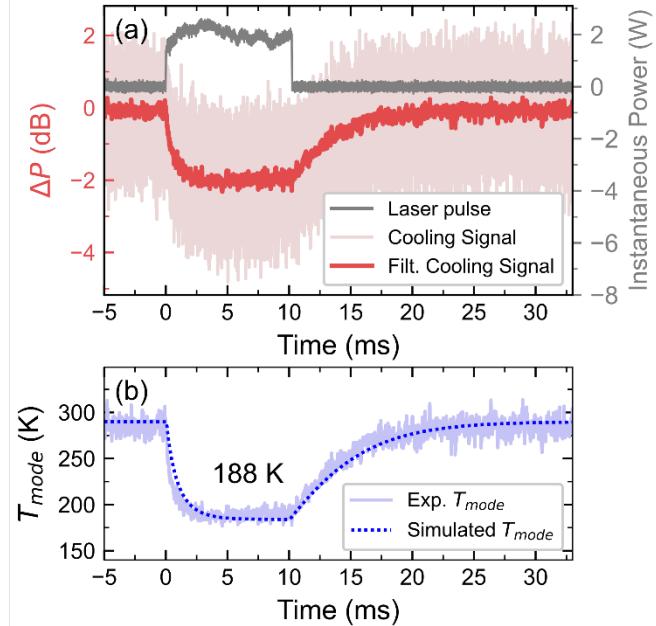
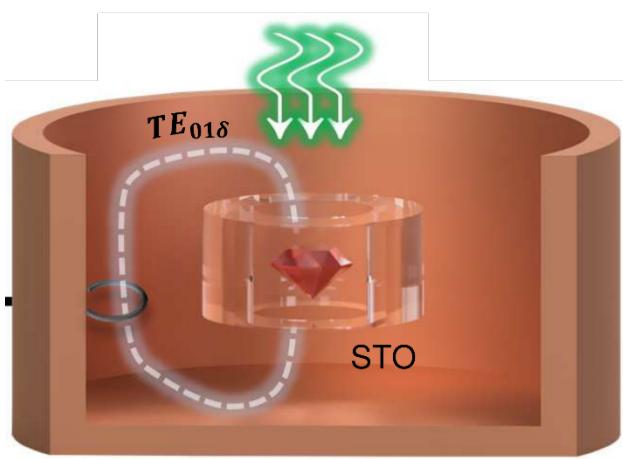
# Zero-field NV<sup>-</sup> diamond as a benchtop microwave mode cooler for reaching the single-photon limit

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Modern solid-state electronic amplifiers (LNAs) enable measurements of rf and microwave frequencies where sensitivity is limited almost entirely by ambient thermal noise, *i.e.*, by the presence of incoherent photons occupying the electromagnetic mode being measured. Significant improvements in sensitivity, so often desperately needed with NMR or EPR scans and imaging, can be achieved by removing these unwanted photons through *cooling* the mode, either during or immediately before a measurement is performed. Conventionally, this is done by inserting the whole NMR/EPR cavity (and sample within it) into a refrigerator or cryostat. We here propose a radical alternative that exploits a strongly absorptive transition in optically-pumped NV<sup>-</sup> centers in diamond to remove thermal photons [1]. Our setup works completely “on a benchtop” with no need for refrigeration or applied magnetic fields, *i.e.*, room-temperature, zero-field (ZF) operation. The required pumping is provided by a continuously operating (CW) green laser. Our experiments showed a measured reduction in the cavity’s noise temperature from 290 K down to 188 K (a drop of more than 100 K), providing a clearly visible reduction in the signal noise. The relative advantages and disadvantages of NV<sup>-</sup> diamond for mode cooling over other polarizable materials (like pentacene-doped *para*-terphenyl [2]) will be explained. Furthermore, we will discuss how improved versions of our mode cooler might be used to reach the single-photon limit and achieve ultra-low-noise quantum measurements at room temperature.



[1] W. Ng *et al.*, *Appl. Phys. Lett.* **119**, 234001 (2021)

[2] H. Wu *et al.*, *Phys. Rev. Lett.* **127** (5), 053604 (2021)

## Disproportionation Reaction of 6,7,8-Trimethylillumazine Investigated by photo-CIDNP

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Cryptochromes and photolyases are members of the same flavoprotein family, abbreviated CPF, which are blue light and ultraviolet-A receptors [1]. Flavin cofactors are critical for signal transmission in these proteins as they can undergo light-induced one and two electron transfer reactions [2]. Investigation of different oxidation states of involved flavin analogues is necessary for understanding the initial step of signal transmission. In a recently described subclass of CPF, a 6,7-dimethyl-8-ribityllumazine (DLZ) chromophore was found in addition to a flavin adenine dinucleotide (FAD) cofactor and a [4Fe-4S] cluster [3, 4]. DLZ, the direct biosynthetic precursor of riboflavin [5], is assumed to be an antenna chromophore by exciting the FAD cofactor [4]. In order to understand the exact mechanism of excitation and energy transfer in the initial step of signal transmission, it is critical to obtain information on the redox chemistry and photochemistry of DLZ and its analogues.

A versatile tool to investigate mechanisms in the context of light-induced radical pair reactions is photo-chemically induced dynamic nuclear polarization (photo-CIDNP). This NMR technique allows the investigation of transient radical pairs that are difficult to probe by EPR. Crucial for this process is a spin-correlated radical pair (SCRP) undergoing nuclear spin dependent intersystem crossing which leads to a process of spin-sorting. The resulting hyperpolarization pattern of the diamagnetic product is proportional to isotropic hyperfine coupling constants of the respective paramagnetic intermediate when a time-resolved experiment is employed. Additionally, the sign of the hyperpolarization is dependent on the multiplicity of the precursor and successor species of the SCRP. Analysis of this range of information provides important mechanistic details of the investigated radical pair reactions [6].

For DLZ and its analogue 6,7,8-trimethylillumazine (TML), an extraordinarily high C-H acidity of the methyl group at position 7 is reported [7]. More recently, TML and its respective anion  $\text{TML}^-$  were found to undergo an unusual light-induced disproportionation reaction involving formation of a SCRP [8]. By means of a photo-CIDNP study, hyperfine coupling constants of the intermediate SCRP were extracted and correlated with predictions from density functional theory. From these findings it was concluded that after light-induced excitation of neutral  $\text{TMLH}$  into a triplet state, subsequent electron transfer from  $\text{TML}^-$  yields the radical species  $\text{TML}^\cdot$  and  $\text{TMLH}_2^\cdot$ . The latter undergoes protonation to form  $\text{TMLH}_2^\cdot$  protonated at N1.

## References

- [1] A. R. Cashmore *et al.*, *Science* **284**, 760-765 (1999)
- [2] V. Massey, *Biochem. Soc. Trans.* **28**, 283-296 (2000)
- [3] F. Zhang *et al.*, *Proc. Natl. Acad. Sci. USA* **110**, 7217-7222 (2013)
- [4] Y. Geisselbrecht *et al.*, *EMBO Rep.* **13**, 223-229 (2012)
- [5] G. W. E. Plaut *et al.*, *Methods Enzymol.* **18B**, 515-538 (1971)
- [6] Y. Okuno *et al.*, *eMagRes* **6**, 283-314 (2017)
- [7] D. H. Bown *et al.*, *J. Org. Chem.* **51**, 2461-2467 (1986)
- [8] J. Wörner *et al.*, *Magn. Reson.* **2**, 281-290 (2021)

## Red-shifted Radical Exciplex on Peptoid Scaffold

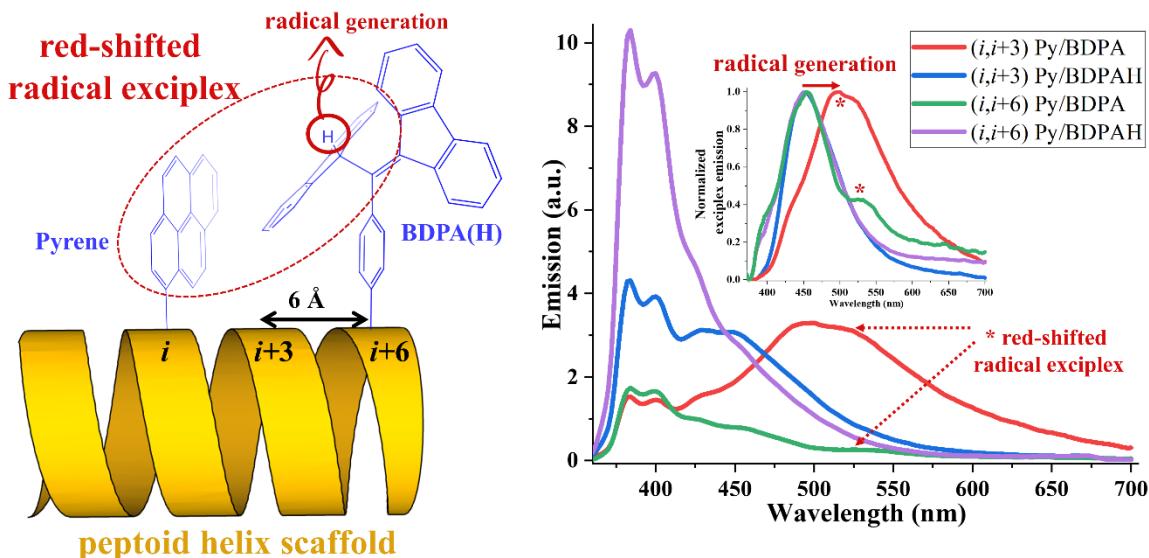
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Exciplex is emissive complex via photoinduced electron transfer (PET) that occurs preferentially in co-facial geometry that can be achieved by taking advantage of the secondary helical structure of peptoid scaffold [1]. In our previous work, the peptoid-conjugated phenanthrene - *N,N*-dimethylaniline exciplex system has been used to investigate the exciplex dynamics and magnetic field effect at various distances and relative orientations between them [2].

In this work, we developed a new peptoid-conjugated exciplex system: a stable radical exciplex. A stable radical,  $\alpha,\gamma$ -bis-diphenylene- $\beta$ -phenyl allyl (BDPA $\cdot$ ) and pyrene (Py) are conjugated on peptoid scaffold at controlled distance. An additional red-shifted peak at 530 nm is observed in radical exciplex (Py and BDPA $\cdot$ ) whereas the conventional non-radical exciplex (Py and BDPAH) exhibits an emission peak only at 454 nm. The exciplex peak at 530 nm is anticipated to be related to spin dynamics, which will be discussed based on the steady-state and time-resolved spectroscopic data.



[1] B. Kang *et al.*, *Org. Lett.* **15**, 1670 (2013)

[2] D. Kim *et al.*, *J. Phys. Chem. Lett.* **11**, 4668 (2020)



## Isotope substitution effects on the magnetic compass properties of cryptochrome-based radical pairs

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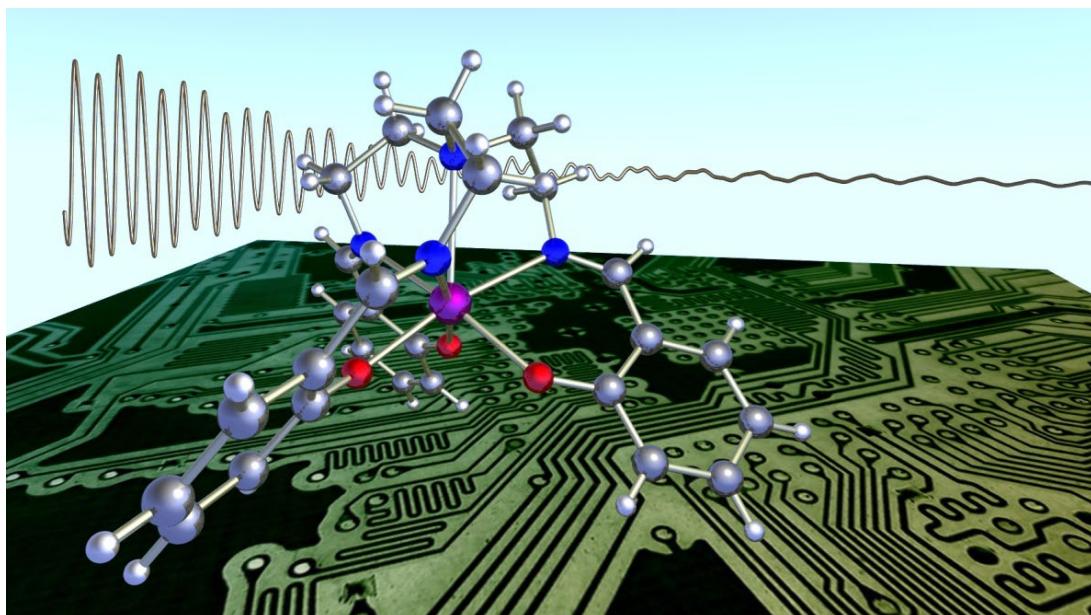
The biophysical mechanism of the magnetic compass sense of migratory songbirds is thought to rely on the photochemical reactions of flavin-containing radical pairs in cryptochrome proteins located in the birds' eyes. A consequence of this hypothesis is that the effect of the Earth's magnetic field on the reaction product yields should be sensitive to isotopic substitutions that modify the hyperfine interactions in the radicals. In this report, we use spin dynamics simulations to explore the effects of  $^1\text{H} \rightarrow ^2\text{H}$ ,  $^{12}\text{C} \rightarrow ^{13}\text{C}$  and  $^{14}\text{N} \rightarrow ^{15}\text{N}$  isotopic substitutions on the functioning of cryptochrome 4a as a magnetic direction sensor. Two main conclusions emerge. (1) Perdeuteration of the flavin chromophore appears to be the best way to boost the anisotropy of the magnetic field effect and to change its symmetry. (2)  $^{13}\text{C}$  substitution of three of the 12 flavin carbons, in particular C4, C4a, and C8 $\alpha$ , seems to be the best way to attenuate the anisotropy. Once spectroscopic techniques are available for measuring magnetic field effects on oriented protein samples, these predictions should give insight into the factors that control the magnetic sensitivity.

## Molecular Lanthanide Complexes for Quantum Technologies

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**Figure 1** Illustration depicting the quantum coherence properties of Yb(trensal) and its suitability for surface deposition in view of its potential use in Quantum Technologies.

We have shown, in collaboration with many co-workers, that molecular Lanthanide-based coordination complexes hold potential for use as physical supports for the implementation of quantum bits and quantum gates in Quantum Information Technology devices. We studied the coherent dynamics of electronic and nuclear spins in Yb(trensal), by pulsed magnetic resonance experiments on oriented single-crystals.<sup>1,2</sup> The coupled electronic qubit-nuclear qudit nature of this system allowed to propose a scheme for intrinsic implementation of efficient quantum error correction schemes.<sup>2</sup> In further work, we investigate the multifrequency single crystal c.w.- and pulse EPR spectra of Gd(trensal), to characterize the energy spectrum and coherent magnetisation dynamics of its  $^8S_{7/2}$  ground term.

[1] K. S. Pedersen *et al.*, *J. Am. Chem. Soc.*, **138**, 5801 (2016).

[2] R. Hussain *et al.*, *J. Am. Chem. Soc.*, **140**, 9814 (2018).

## Spin-Correlated Radical Pairs in Avian Cryptochromes

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Cryptochromes are photoreceptor proteins that are believed to be key to the magneto-receptive ability of night-migratory songbirds. Upon blue-light illumination a non-covalently bound flavin cofactor is excited, initiating an electron transfer cascade along a series of nearby tryptophan residues, Fig. 1. Ultimately, a radical pair between the flavin cofactor and a terminal tryptophan residue is formed.

The radical pair formed under conservation of total spin angular momentum is spin-correlated, as the initially generated singlet radical pair is not an eigenstate of the total spin Hamiltonian. The resulting, hyperfine coupling-driven, coherent singlet-triplet interconversion of the radical pair is sensitive to magnetic fields of the order of mT.

A plethora of optical and EPR-based spectroscopic methods can be utilised to study these systems.[2] EPR is of particular importance as the precise identity of any spin-correlated radical pairs formed can be determined; interactions that drive magnetosensitivity, such as hyperfine couplings, can also be characterised. In this work, out-of-phase electron spin echo envelope modulation (ESEEM) and transient EPR (TrEPR) are the principal techniques used to study cryptochrome radical pairs.

Out-of-phase ESEEM is a pulsed EPR technique used to probe the inter-electron spin couplings. Determination of these interactions, in particular the dipolar coupling, to a high degree of accuracy allows for the separation between radicals to be calculated.

Many interaction parameters influence the shape of TrEPR spectra of spin-correlated radical pairs. Using a home-written simulation routine these parameters, such as the g-values and hyperfine couplings of each constituent radical, can be extracted.

In this work wildtype and proteins with single-point mutations from a variety of organisms are investigated, with the above techniques combining to unambiguously identify the radical pairs formed.

[1] C. Levy *et al.*, *Nature*, **495**, 7441 (2013)

[2] J. Xu *et al.*, *Nature*, **594**, 535-540 (2021)

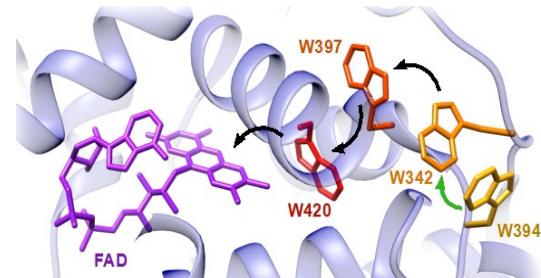


Figure 1: X-ray structure of radical pair region for *Drosophila melanogaster* cryptochrome. [1]



## Spin Counting by Pulsed EPR Methods

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The oligomeric stoichiometry of membrane protein complexes is important for their biological function and often depends on the lipid composition. EPR can measure such protein complexes in their native environment. If each of the protein units is single spin-labeled, pulsed EPR methods allow to determine the number of coupled spins. We have shown in the past that the modulation depth of the Pulsed Electron-Electron Double Resonance experiment (PELDOR or DEER) is sensitive to the number of coupled spins [1,2]. More recently, we could also demonstrate that for trityl spin labels with a narrow EPR line width, multi-quantum filtering can be used to determine the oligomeric state [3], similar as it is done in NMR. In both cases, we investigated model compounds or protein complexes with up to 4 dipolar coupled electron spins. Here we will report on new pulsed EPR experiments performed with shaped broadband microwave pulses to determine the number of dipolar coupled electron spins on multi-nitroxide molecules (with up to 6 nitroxide units synthesized in our group). Accuracy and limitations of the spin counting procedure will be discussed with respect to the dipolar coupling strength, the spectral width and the number of coupled spins.

### References

- [1] Bode, B. E., Margraf, D., Plackmeyer, J., Dürner, G., Prisner, T. F. and Schiemann, O. Counting the Monomers in Nanometer Sized Oligomers. *J. Am. Chem. Soc.*, 129, 6736 – 6745 (2007)
- [2] Endeward, B., Butterwick, J. A., MacKinnon, R. and Prisner, T. F. Pulsed Electron-Electron Double-Resonance Determination of Spin-Label Distances and Orientations on the Tetrameric Potassium Ion Channel KcsA. *J. Am. Chem. Soc.*, 131, 15246 – 15250 (2009)
- [2] Bretschneider, M., Spindler, P. E., Rogozhnikova, O. Yu., Trukhin, D. V., Endeward, B., Kuzhelev, A. A., Bagryanskaya, E., Tormyshev, V. M. and Prisner, T. F., Multiquantum Counting of Trityl Radicals. *J. Phys. Chem. Lett.*, 11, 6286-6290 (2020)

## Selective isotope labelling of tyrosine in flavoproteins for $^{13}\text{C}$ solid-state photo-CIDNP effect

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Low sensitivity remains a major limiting factor for the wide applications of nuclear magnetic resonance (NMR) spectroscopy in different areas. The chemically induced dynamic nuclei polarization (CIDNP), which generates non-Boltzmann nuclear spin magnetization, is one of the hyperpolarization methods allowing for sensitivity enhancement in NMR [1]. Several studies have investigated the solid-state photo-chemically induced dynamic nuclear polarization (photo-CIDNP) effect in the flavoprotein system, however the mechanisms underlying this effect have yet to be fully understood [2,3]. Here we study the photo-CIDNP effect observed in the tryptophan-lacking light-oxygen-voltage (LOV) domain 4511 from *Methylobacterium radiotolerans* (Mr4511) [4], the mutant Mr4511-C71S was synthesized with  $^{13}\text{C}$  selective isotope labelling of tyrosine. The mutant Mr4511-C71S carries a flavin mononucleotide (FMN) and the reactive cysteine is mutated into a serine. After being measured by  $^{13}\text{C}$  MAS NMR under illumination, a strong CIDNP signal was observed, indicating that the tyrosine acts as electron donor and forms a radical pair with FMN. which leads to the photo-CIDNP effect.

## References

- [1] Kuhn, L. T. *Hyperpolarization methods in NMR spectroscopy*. (Springer, 2013).
- [2] Wang, X. J *et al.*, *Wuli Huaxue Xuebao/ Acta Phys. - Chim. Sin.* **32**, 399–404 (2016). DOI: 10.3866/PKU.WHXB201511272.
- [3] Smitha S. T. *et al.*, *J Am Chem Soc*, 15542-15543(2010). DOI: 10.1021/ja1082969.
- [4] Y. Ding, *et al.*, *Sci. Rep.* **10**, 1–13 (2020). DOI: 10.1038/s41598-020-75627-z.

## Room temperature magnetic sensing using a molecular compass – a magnetic resonance and field effect study

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Donor–acceptor molecular triad systems are known to possess long-lived photogenerated charge-transfer states. Such systems are highly applicable in investigations of artificial photosynthesis and magnetic sensing [1–3]. In this contribution we report on our investigations of a perylene donor, and naphthalene-1,4:5,8-bis(dicarboximide) secondary acceptor triad (Per-Xy-NMI-*p*-NDI), studied using electron paramagnetic resonance (EPR) and sub-ns transient absorption (TA) spectroscopies. Temperature-dependent transient cw and pulse EPR methods were used to elucidate the magnetic parameters of both the charge-transfer radical-pair and local-exciton recombination triplet states, as well as the recombination kinetics between them. TA performed in magnetic fields, with magnitudes spanning from Earth strength to tens of mT, yield double differential absorption spectra. These data demonstrate a long-lived charge-transfer state with both high absolute and relative magnetic-field effect. At 298 K the magnitude and sign of the field effects are acutely sensitive to varying solvent conditions, driven by the strong dependence of radical-pair energetics on the dielectric constant of the solvent. EPR data and simulations are interpreted in the context of quantum chemical calculations and TA transients are modelled using quantum mechanical simulations.

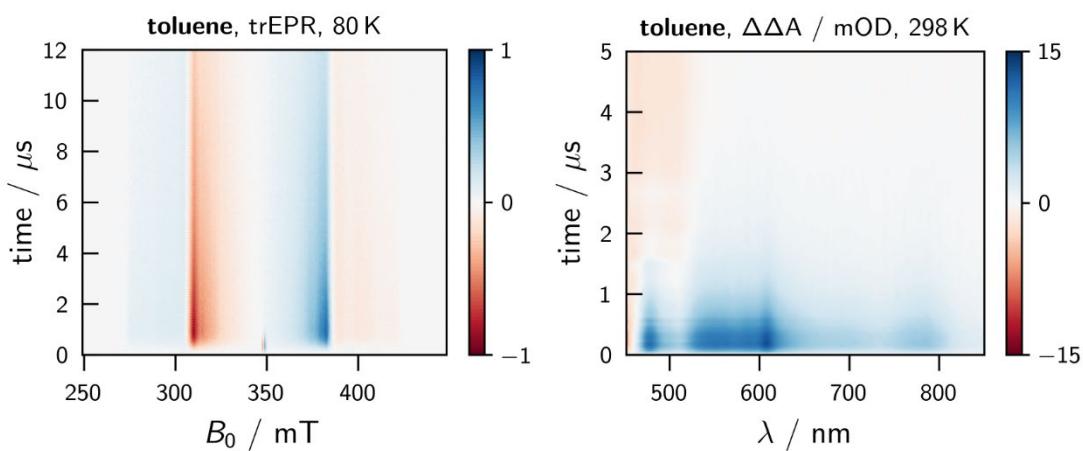


Figure 1: trEPR and TA matrix data frame projections for Per-Xy-NMI-*p*-NDI in toluene

[1] Kerpál, C.; Richert, S. et al., *Nat. Commun.*, **10**, 3707 (2019)

[2] Han, W.-S. et al., *Tetrahedron*, **73**, 4925–4935 (2017)

[3] Carbonera, D. et al., *J. Am. Chem. Soc.*, **120**, 4398–4405 (1998)



## **Photonic Band-Gap Resonators for High Field EPR and DNP NMR of Thin Film Spintronic Materials**

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Characterization of thin film materials and spin systems imposes several unique challenges on designing EPR and NMR experiments. One is the sample geometry that results in rather poor filling factors and, thus, poor signal-to-noise when using conventional EPR or NMR probeheads optimized for cylindrical sample tubes. This issue is becoming particularly challenging for EPR at or above 95 GHz (W-band) because of the sample tube diameter falling below ca. 0.9 mm and difficulties with sample handling. Another issue arises in non-resonant dielectric losses associated with irradiating samples at these mm-Wave (mmW) frequencies. The latter losses represent another obstacle for expanding DNP technology to room temperature experiments with at least some of the samples. Recently, we introduced mmW resonators for EPR and DNP that are based on one-dimensional photonic band-gap (PBG) structures [1, 2]. Such resonators are formed by stacks of flat plates with alternating dielectric constants (high,  $\epsilon_2$  and low,  $\epsilon_1$ ) and thicknesses corresponding to  $(2m+1)\lambda/4$ , where  $m=0, 1, 2\dots$  and  $\lambda$  is the mmW wavelength in the dielectric material. A defect in such a 1D photonic crystal, such as, for example, formed by a flat metallic mirror with a sample on top of it, confines mmW into a resonant structure [1]. The optimal sample thickness is  $\lambda/4$  for lossy samples (this could be increased for non-lossy materials) while the sample diameter is generally limited only by the available space in a magnet (for EPR) or considerations for an efficient NMR coil (for DNP). Thus, such geometry is uniquely suitable for thin film samples and an integration with NMR detection [2]. Here we describe the recent progress in developing a series W-band PBG resonators with  $Q$ -factor up to  $\approx 3,400$  for EPR and then  $Q \approx 500$  resonators integrated into DNP NMR probe operating at 197 GHz EPR and 300 MHz  $^1\text{H}$  NMR frequencies. By using home-build all solid-state quasioptical 197 GHz bridge ( $\approx 0.5$  W output power), DNP enhancements up to  $\approx 2,000$  were observed for natural abundance  $^{13}\text{C}$  NMR signals from HPHT diamond crystals at room temperature. While DNP enhancements for micro- and nanodiamonds were significantly lower, the instrument was fully suitable for characterizing several particulate diamond materials including thin ( $\approx 3$  mil thick) 3M<sup>TM</sup> 666XW polyester-based lapping film containing  $\approx 6$  wt% of 1  $\mu\text{m}$ -diameter diamond particles [3]. We have also examined magnetization buildup for a series of diamond powders fabricated to optimize properties on NV-centers. Supported by NIH 5R01GM130821.

### **References**

- [1] S. Milikisyants *et al.*, *J. Magn. Reson.* **296**, 152 (2018)
- [2] A. Nevzorov *et al.*, *J. Magn. Reson.* **297**, 113 (2018)
- [3] A. Nevzorov *et al.*, *J. Magn. Reson.* **323**, 106893 (2021)

## **Elucidating quantum coherence in the complex system of the avian compass**

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Quantum coherence has been suggested as a resource that nature may utilise in the spin dynamics of the hypothesised radical-pair mechanism of the avian compass. Whilst theoretical studies have provided insight [1,2], they often assume a small number of coupled nuclei in the radical-pair and thus lack sufficient complexity of the biological system. Here, we investigate realistically large radical-pair models with up to 21 nuclear spins, inspired by the magnetic field sensitive protein cryptochrome [3]. By varying relative radical orientations, we reveal correlations of several coherence measures [4] with compass sensitivity. Whilst electronic coherence is found to be an ineffective predictor of compass sensitivity, in some cases producing a strong anti-correlation, a robust correlation is established with a measure of the global coherence of electron and nuclear spins [5]. The results demonstrate the importance of realistic models, and appropriate choice of coherence measure, in elucidating the quantum nature of the avian compass [6].

- [1] I. K. Kominis, Phys. Rev. Res. **2**, 023206 (2020).
- [2] R. Jain et al., Proc. R. Soc. A **477**, 20200778 (2021).
- [3] J. Xu et al., Nature **594**, 535 (2021).
- [4] T. Baumgratz, M. Cramer, and M. B. Plenio, Phys. Rev. Lett. **113**, 1 (2014).
- [5] J. Cai and M. B. Plenio, Phys. Rev. Lett. **111**, 230503 (2013).
- [6] L. D. Smith, J. Deviers, and D. R. Kattnig, Sci. Rep. **12**, 1 (2022).

## MolSpin – Introducing a versatile software package for spin chemistry

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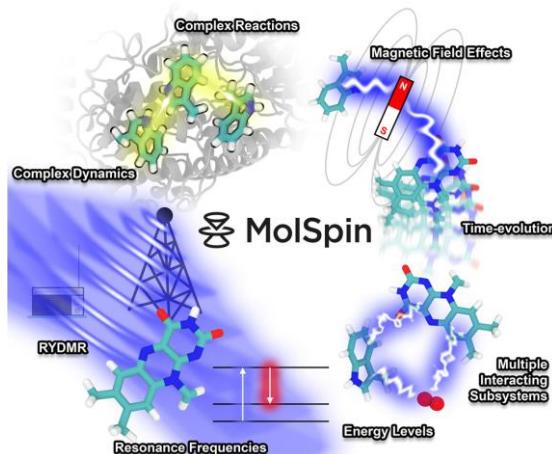
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Spin-dependent chemical reactions reveal fascinating mechanisms which are of high interest in the current scientific community. For instance, the application of an external magnetic field would affect the yield in simple radical reactions of formic acid formation [1]. Furthermore, spin-dependent reactions are believed to be the fundamental cause for endowing migratory birds with the ability to sense the Earth's magnetic field [2]. It is thus important to understand and describe the dynamics and interactions of spin systems of varied complexity. Not only the interactions between spins but also the influence of the environment exhibits an important aspect which leads to observable effects in experiments. The underlying theoretical framework to describe these effects relies on the Liouville-Von-Neumann equation. However, the solution of this equation is in most cases not only challenging for realistic systems but also requires the utilization of supercomputers.



**Figure 1** Examples of problems that can be described by MolSpin [3].

We have developed the software package MolSpin to efficiently solve and investigate spin dynamics for spin chemistry problems [3]. With MolSpin it is possible to describe spin-dependent reaction mechanisms, the influence of molecular motion and other perturbations using the Bloch-Redfield-Wangness formalism, and several other features. The software package is built to allow for an easy implementation of additional tasks and is thus suitable for challenging problems related to spin dynamics.

[1] T. C. Player, *J. Chem. Phys.*, **153**, 084303 (2020).

[2] J. Xu *et al.*, *Nature*, **594**, 535-540 (2021).

[3] C. Nielsen *et al.*, *J. Chem. Phys.*, **151**, 194105 (2019).

# The influence of dynamical degrees of freedom on compass sensitivity: A comparison of plant and migratory bird cryptochromes

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The magnetic compass of migratory birds is thought to rely on the radical pair mechanism operating inside a cryptochrome blue-light photoreceptor [1]. It is imperative that the radical pair exists in a nonequilibrium coherent state long enough for the Earth's magnetic field to have an influence on the underlying coherent spin dynamics. Fluctuations of pertinent interactions weaken the coherence of the radical pair in a process called spin relaxation [2]. Here, we investigate the dynamical properties of relevant dihedral and librational angles in the flavin adenine dinucleotide ( $\text{FAD}^{\cdot-}$ ) and tryptophan ( $\text{Trp}^{\cdot+}$ ) radical pair inside cryptochrome 4a from European robin (*ErCry4a*) and cryptochrome 1 from *Arabidopsis thaliana* (*AtCry1*) to characterise the implications of thermal motion on compass sensitivity. This analysis relies on the time-dependent hyperfine interactions in the  $\text{FAD}^{\cdot-}$  and  $\text{Trp}^{\cdot+}$  radicals, which permit calculation of the quantum yield anisotropy of the radical pair recombination influenced by an external magnetic field. The quantum yield anisotropy is a measure for the sensitivity of the birds' magnetic compass. The quantum yield anisotropy and dynamical parameters were compared for radical pairs in *ErCry4a* and *AtCry1* to determine whether evolutionary optimization of motional degrees of freedom in the avian radical pair could lead to a significantly better detection of the magnetic field.

## References

- [1] J. Xu et al., *Nature*, **594**(7864), 535–540 (2021)
- [2] D. Kattnig et al., *Phys. Chem. Chem. Phys.* **18**, 12443–12456 (2016)

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### **A Wavepacket Picture of Electron and Spin Transfer**

The dynamics of electron transfer are complicated in the presence of spin, whereby one must consider more than two electronic states and there are modifications to the usual Marcus/Hush/Jortner formalism; for instance, there are clear indications that there can be strong spin preferences in electron transfer events and that the nuclear dynamics can be spin dependent. At the same time, there are very few theoretical approaches for describing spin transfer concomitant with electron transfer/electronic relaxation. As an example, one cannot run surface hopping dynamics because there are so many degenerate states and the Hamiltonian is complex-valued (which leads to novel Berry forces).

Here, I will highlight a new phase-space approach for treating electron transfer with spin based on transforming all dynamics to a moving frame and then making a semiclassical approximation. I will show thereafter that spin-polarized wavepackets emerge naturally in the context of nonequilibrium photo-excitation and electron transfer, and that the nuclear dynamics follow a built-in magnetic field. I will also show that these built-in magnetic fields lead to spin-dependent nonequilibrium dynamics.

Finally, I will highlight how this coupled nuclear-electronic-spin interaction may well play a role in chiral induced spin selectivity likely among many other spin-related phenomena.

### **References should be listed as below**

- [1] X Bian, Y Wu, HH Teh, JE Subotnik *JCTC* **18**, 2075-2090 (2022)
- [2]. Y. Wu and J.E. Subotnik *J. Chem. Phys.* **154**, 234101 (2021)
- [3]. X. Bian, Y. Wu, H.H. Teh, Z. Zhou, H.T. Chen, J.E. Subotnik. *J. Chem. Phys.* **154**, 110901 (2021)
- [4]. Y. Wu, J.E. Subotnik *Nat. Comm.* **12**, 1-7 (2021)

## Coherent Control of Radical Species

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Design of laser waveforms optimized for reaction control has attracted theoretical and experimental attention.[1] However, it is not easy to realize the designed laser field. In contrast, recent progress of arbitrary wave generator (AWG) enables us to produce the designed radio wave field (RF). Recently, we have shown that it is possible to control the recombination reaction of a radical pair (RP) in high field using radio wave magnetic resonance designed based on the local optimization theory [1,2]. As an example of coherent control, here we show the spin multiplicity control of RP at low fields and the design of optimized AWG pulse that induce selective spin echoes.

Coherent control is control that targets a transient state  $|f\rangle_L$  that is non-eigenstate of the Hamiltonian. In order to realize  $|f\rangle_L$  at specific time  $t_f$ , it is necessary aiming  $|\rho_f\rangle_L$  state that time-evolves to  $|f\rangle_L$ . By using reverse time-evolution operator,  $|\rho_f\rangle_L$  is defined as,

$$|\rho_f\rangle_L = \exp\{i\hat{L}_0(t_f - t)\}|f\rangle_L$$

To perform control,  $|f\rangle_L$  was set as the singlet state in spin multiplicity control and the  $S_y + S_z$  in the spin echo control.

Spin multiplicity control was done in a model RP system having one nuclear spin (HFC A=0.5 mT). In low field, almost all spin states are mixing coherently. We calculated an RF field with the aim of controlling a singlet born RP to singlet state after 1  $\mu$ s. Fig.1B shows the time-evolution of the singlet probability in presence and absence of designed RF field. The RF irradiation change the singlet probability at 1  $\mu$ s after the production of RP from 39 % to 96 %.

As a model system for selective control of spin systems, we assume a system in which TEMPO (solution) and BDPA (solid) are mixed(Fig.(B)). In this system, we designed the waveform so that the TEMPO radical transitions to the  $S_y$  state at the set time (200 ns) while the BDPA radical remains in the  $S_z$  state. By irradiating the designed waveform, we could obtain spin echoes in which the two radical species are clearly separated compared to the case of irradiating multicolor pulses corresponding to the resonance frequency of TEMPO.

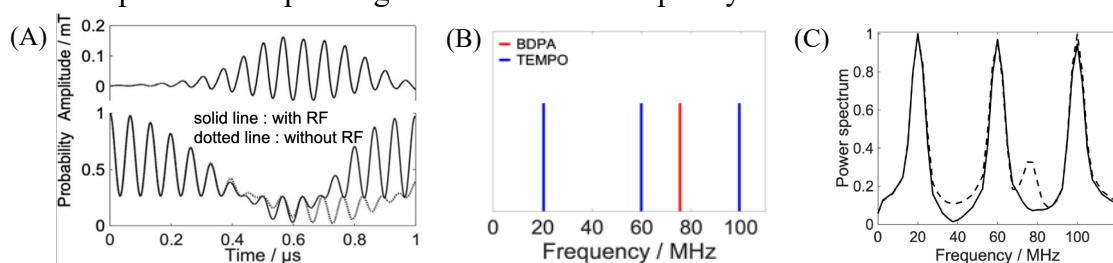


Fig. (A)Upper: Calculated RF, Lower: Time-evolution of singlet probability (B)Model system  
(C)Obtained spin echo after optimized pulse(solid line) and after multicolor pulse(dotted line)

### References:

- [1] M.Sugawara, *J. Chem. Phys.* **118**(15), 6784-6800 (2003).
- [2] K.Masuzawa, M.Sato, M.Sugawara, and K.Maeda, *J. Chem. Phys.* **152**, 014301 (2020)

## Up Close and Personal: Micro-mechanical Resonators as EPR Cavities. Going Beyond the Quasi-static Approximation to Simulate Electromagnetic-Acoustic Coupling in Piezoelectric Devices with Commercial FEM Software

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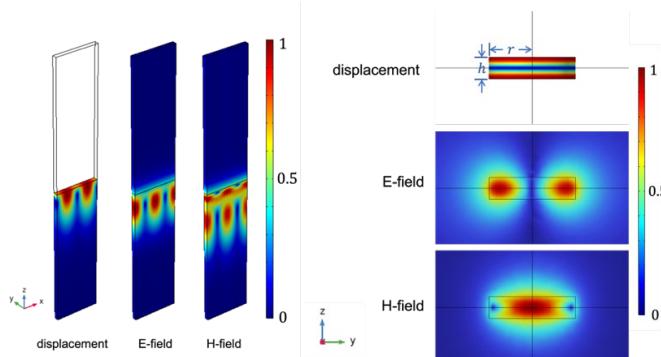
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Regular EPR spectroscopy and masers are powerful methods for exposing and, with care, accurately quantifying the spin dynamics of molecules and materials made from them [1]. But the size of a regular EPR/maser cavity limits its performance and applicability. Since the speed at which mechanical waves (sound) propagate through a material is, in general, vastly smaller than the speed at which electromagnetic waves (light) do, the use of a piezoelectric resonator as the cavity could significantly reduce this. But, before getting too enthusiastic, one needs to work out the location and amplitude of the (microwave) magnetic field that the displacement current within a deforming piezoelectric structure can generate. Numerical computation based on the finite-element methods (FEM) can, in principle, do this. However, conventional FEM software for simulating piezoelectric devices invokes, for simplification, the so-called quasi-static approximation, which completely ignores the magnetic field [2].

We have thus rolled up our sleeves up and developed a new FEM simulation method for piezoelectric devices. This method does not make the quasi-static approximation, so allowing the magnetic field to be accurately simulated. This method is based on weak forms and can be applied to any FEM software like COMSOL. We validate the accuracy and ability of this method in two cases: Rayleigh modes on piezoelectric waveguides (left figure) and torsional modes on cylinder antennas (right figure). This method enables us to calculate the magnetic coupling coefficient (the ratio of magnetic energy to the total energy). Using this coefficient as a guide, we can find the best structure for a micron-scale EPR scanning head or maser cavity.



### References

- [1] Oxborrow et al., *Nature* 488, 353–356 (2012)
- [2] B. A. Auld, *Acoustic Fields and Waves in Solids*. (JOHN WILEY & SONS, New York London, 1973), pp. 298-304

## **Porphyrin-based Triad with Exceptionally High MFE on Phosphorescence**

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Magnetic control over molecular emissivity presents interests for various fields of technology and medicine. We present experiments exploring magnetic field effects (MFE) on phosphorescence in donor-acceptor dyads and triads based on Pt porphyrins (PtP). In one triad, consisting of phosphorescent Pt porphyrin (PtP), rosamine B (RosB) and trialkoxybenzene (TAB), covalently linked together by conductive oligophenylene bridges, photoexcitation leads to two sequential reversible electron transfer processes (ET), generating two radical pairs (RP), respectively. The first rate-limiting ET originates in the local PtP triplet state, and it is slightly endergonic, competing with, but not entirely quenching the PtP phosphorescence. The second ET is exergonic, resulting in the formation of the final RP with large inter-radical distance. The RPs recombine either to the ground state (singlet channel) or back to the emissive PtP triplet state (triplet channel). The net distribution of the RP decay over the recombination channels, and hence the phosphorescence decay time and intensity, are governed by the spin dynamics in the RP(s) and are sensitive to magnetic field. The phosphorescence of the triad was found to exhibit remarkably strong positive MFE with the magnitude reaching up to ~12% in the field of a hand-held toy magnet. A kinetic model was developed that allowed us to reproduce the observed behavior of the triad. Overall, this work constitutes an important step towards the design of magnetically sensitive luminescent materials, which in the future may be exploited in construction of a new kind of biological imaging probes.

## **Spin Trapping Reactive Oxygen Species Produced by X-ray Scintillating Nanoparticles**

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Photodynamic therapy (PDT) is a treatment for cancer that utilizes photoexcitation of a dye to generate singlet oxygen and other reactive oxygen species (ROS) and induce apoptosis of diseased cells. Traditionally, PDT has employed sensitizers responsive to red wavelengths of light. Sensitizers are administered orally, leading to photosensitivity and damage to healthy tissue. X-ray scintillation may provide more targeted treatment and minimize side effects of PDT. Radioluminescent nanoparticles can generate reactive oxygen species following, making them an alternative PDT sensitizer capable of deeper tissue penetration, thereby expanding the use of PDT as a therapeutic agent. Because ROS are short-lived, direct detection methods are not always capable of quantify the amount and chemical identify of any ROS generated. We report results confirming generation of reactive oxygen species from radioluminescent lanthanide-doped nanoparticles coupled to an ROS generating organic dye. Using a variety of spin traps, including some selective for certain ROS, we were able to positively identify at least three different radicals produced in the presence of these nanoparticles following exposure to X-ray radiation.

# A Vector Model for Spin State Mixing in Triplet Pairs

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Triplet pairs are generated by singlet fission or encounters of free triplet excitons in organic crystals [1]. Recently there has been renewed interest in singlet fission and triplet-triplet annihilation because these processes can potentially improve the efficiency of energy conversion in organic devices. Singlet fission and triplet-triplet annihilation are a spin conservative process while spin states can be mixed in triplet pairs. Spin state mixing in triplet pairs is one of the key processes to determine the efficiency of geminate triplet-triplet annihilation in triplet pairs after the initial singlet fission event and of triplet-triplet annihilation in triplet pairs formed by free triplet excitons. Though the concept of triplet pair has been established since 1960s [1], spin state mixing processes in triplet pairs are still unclear because of their complexity.

Magnetic field affects spin state mixing in triple pairs and the efficiency of subsequent triplet-triplet annihilation. The observation of magnetic field effects on triplet pairs has been the most reliable method to prove the singlet fission and triplet-triplet annihilation processes in organic materials. In the absence of a magnetic field, spin states are mixed by dipole-dipole coupling in a triplet. In the presence of a high magnetic field, the Zeeman interaction largely separates the energies of spin states, preventing state mixing between spin states. In the case that magnetic field is comparable with dipolar coupling in a triplet, spin state mixing is known to be enhanced though the mechanism of the enhancement is unclear. These spin state mixing processes are complex and analytical expression for the spin state mixing in triplet pairs has not been available.

In the present study [2], an analytical model based on three state mixing is developed to study spin state mixing in triplet pairs using the density operator formalism. In the model, a triplet pair is generated by singlet fission and is assumed to be recombined to the singlet state (geminate triplet-triplet annihilation via singlet channel). The spin Hamiltonian comprises of dipole-dipole coupling in a triplet and the Zeeman interaction of electron spins. The time evolution of the singlet population in the triplet pair is calculated with the Liouville von Neumann equation. The singlet population in the triplet pair oscillates with respect to time due to the coherent spin state mixing in the triplet pair. The number, amplitudes and frequencies of the oscillations are dependent on the applied magnetic field. An analytical expression for the spin state mixing in the triplet pair is developed from the magnetic field dependence of the oscillations. The analytical calculations are identical with numerical calculations when two triplet excitons are identical, and the magnetic field direction is parallel to one of the principal axes for the dipolar coupling in a triplet exciton. A simple vector model based on the three states mixing is proposed to understand the spin state mixing in triplet pairs [2].

## References

- [1] R. E. Merrifield, *Pure Appl. Chem.* **27**, 481 (1970)
- [2] T. Yago., *J. Chem. Phys.* **151**, 214501 (2019)

## Reduction of thymine radicals by Tryptophan: A study of CIDNP kinetics**bold**

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As model for a reaction mimicking a chemical DNA repair process, the reduction of short-lived thymine radicals by tryptophan and N-acetyl tryptophan in a wide pH range in aqueous solution was investigated. To generate the radicals pulsed laser irradiation was implemented to a solution containing the photosensitizer 3,3',4,4' -tetracarboxy benzophenone (TCBP), thymine, and tryptophan or N-acetyl tryptophan. As a preliminary step, the photoinduced oxidation of thymine by triplet-excited 3,3',4,4' -tetracarboxy benzophenone was studied and thymine radical intermediates were characterized by means of time-resolved chemically induced dynamic nuclear polarization (CIDNP). It was shown that proton-coupled electron transfer (PCET) from neutral thymine to the triplet excited photosensitizer in neutral aqueous solution (pH 6.3) leads to the formation of a neutral thymine radical; its formation is preceded by the formation of an elusive cationic thymine radical on the geminate stage of the reaction. In contrast, in basic solution (pH 11.7) a thymine anion reacts with the triplet excited photosensitizer by electron transfer resulting in the formation of a TCBP radical anion and a neutral thymine radical. The latter deprotonates rapidly, and a thymine radical anion is formed at these conditions. To determine the rate of the reduction reaction between tryptophan and its N-acetyl derivative and the neutral thymine radical (pH 6.3) or the thymine radical anion (pH 11.7) the CIDNP kinetics obtained in the photoreaction of TCBP and thymine with and without adding a reducing agent were simultaneously analyzed quantitatively. As a result, the second order rate constants of the reduction reaction,  $k_r$ , were determined:  $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH 6.3 and  $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at pH 11.7 for N-acetyl tryptophan;  $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH 6.3 and  $4.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at pH 11.7 for tryptophan.

The experimental part of this work was supported by Russian Science Foundation (project no. 20-63-46034) and the theoretical modelling was supported by the Ministry of Science and Higher Education of the Russian Federation (Grant No. 075-15-2021-580).



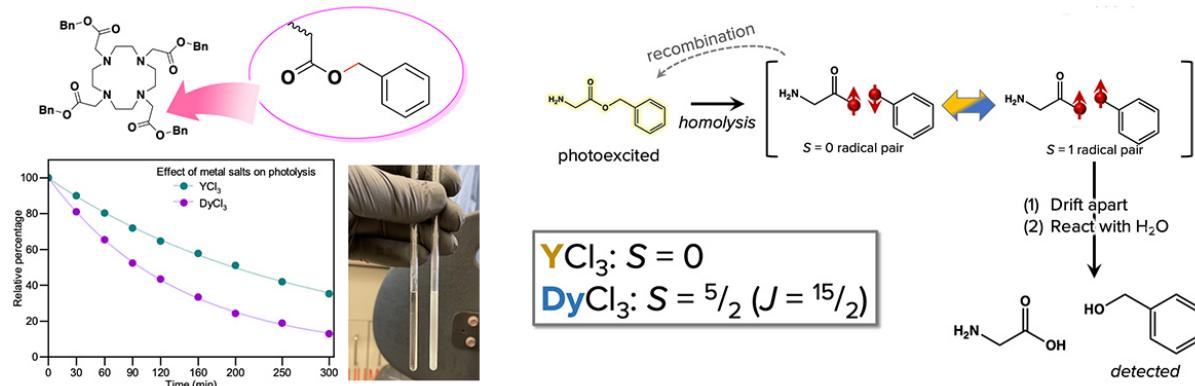
## Rare-Earth Magnetic Control of Photolysis Reactions

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Rare-earth elements are essential in modern technology. Yet, their chemical separations and purification is a complicated procedure because the typical thermodynamic quantities (e.g. solubility or ionic radius) vary only gradually, producing inefficient separations processes. Magnetic properties, in contrast, vary starkly across the rare-earth elements, and developing means of harnessing magnetism to separate them is of prime importance.

In this talk, we will cover our approach to harnessing the electronic spin of the rare-earths for a reactive separations procedure that exploits a magnetic effect on radical-pair reactions<sup>1</sup> for the separations handle. Turro and coworkers, as well as Sakaguchi, showed three decades ago that rare earths can modify the outcomes of chemical reactions that incorporate these radical pairs.<sup>2,3</sup> Yet the exact magnetic parameters responsible for that control e.g. spin ground state, bulk magnetic moment, or spin relaxation time, among others, are still undefined.

We are currently designing ligand shells to both provide that understanding and enable tests of chemical separations. We are specifically targeting predominantly O- and N-atom donor chelate backbones, with radical-pair forming groups appended to them. As an initial proof of concept, we are studying the role that magnetic rare earths play in governing the photolysis of benzyl esters, specifically benzylglycine, which will comprise the radical-pair forming groups we eventually append to the ligand scaffolds (**Fig. 1**). Results in this area will be discussed.



**Fig. 1.** Summary of results, target chemical system, and spin catalysis.

### References.

- [1] Steiner U. et. al., *Chem. Rev.* **89**, 51 (1989)
- [2] Turro N. et. al., *Chem. Phys. Lett.* **120**, 397 (1985)
- [3] Sakaguchi, Y. et. al., *Chem. Phys. Lett.* **106**, 420 (1984)
- [4] Buchachenko, A. et. al., *Chem. Rev.* **102**, 603 (2002)

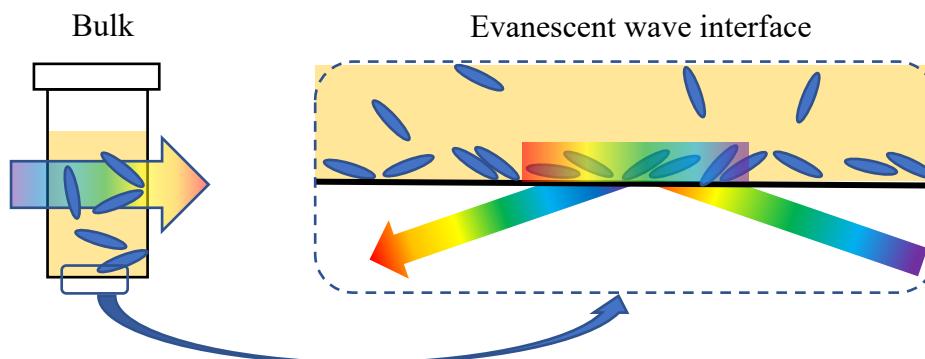
## Exploring surface aggregation and magnetic field effect of biological molecules via polarization-sensitive evanescent wave spectroscopy

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Optical spectroscopy is an indispensable tool in studying and understanding the mechanisms of chemical reactions by tracing the loss of reactants, the production of products or the concentrations of reactive intermediates in real time. Over the past years our group has developed various spectroscopic methods to detect the magnetic field effect(MFE) of unoriented biological molecules in bulk[1]. By ignoring the large bulk phases above the surface, the evanescent wave(EW) variant method offers a solution to reduce the dimensionality, typically it monitors the interface and reflects the orientation of molecules through the difference in S/P polarizations.



In measuring MFEs that occur in the spin-correlated radical pair systems, there are two main challenges: (1) to attract the interfacial molecules. The behaviour of molecules at interfaces is often drastically different to that in bulk solution, some adsorbed species can aggregate and therefore show an orientational angle. For different biomolecules, we have designed specific landing schemes at the silica/water interface. (2) to boost sensitivity of detection. The  $1\mu\text{m}$ -thin EW layer brings less absorbance compare with bulk measurements, leading to a higher requirement of sensitivity.

Here we will present the latest developments of the polarization-sensitive evanescent wave spectroscopy, and its application in detecting photo-induced MFEs from Thionine/DABCO model system to the protein of a migratory bird cryptochrome.

### Reference

- [1] Xu J, Jarocha L E, Zollitsch T, et al. Magnetic sensitivity of cryptochrome 4 from a migratory songbird[J]. Nature, 2021, 594(7864): 535-540.

**Spin dynamics simulation package  
for fixed-geometry charge-  
separated systems**

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Charge-separated radical intermediates of photoinduced chemical reactions with rather rigid molecular geometry and strong coupling between unpaired electrons participate in various important processes, for example, in photosynthesis of plants [1]. It is tempting to construct an artificial organic photosynthetic system which is mimicking the processes in the natural one to tackle the world's growing energy consumption challenge in a "green" way. This requires deep understanding of photochemical processes taking place both in natural and artificial systems. Both coherent and incoherent spin selective processes strongly affect the chemical properties of such charge-separated states, thus modulating the efficiency of the overall processes [2], but sometimes it is difficult to separate the influence of different processes involved. Experimental methods developed in spin chemistry: magnetic field affected reaction yield (MARY), chemically induced electron and nuclear polarization (CIDEP and CIDNP, correspondingly) can be applied to disentangle contributions from different channels, but they are effective only in combination with thorough analytical and numerical calculations.

In this contribution, the newly written Matlab based script package will be introduced, which allows to calculate the magnetic field effect of any observable, including CIDNP [3], CIDEP, MARY [4], and is freely available on request. It has been successfully applied for simulating proton and carbon-13 solution-CIDNP field dependences of a series of donor-linker-acceptor systems with at least 23 magnetic nuclei with non-zero hyperfine coupling in charge-separated state [3]. Its architecture and approximations made will be described, and the influence of model parameter's variations will be shown.

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## References

- [1] K. Möbius, *Chem. Soc. Rev.* **29**, 129 (2000)
- [2] J. Schäfer *et al.*, *Phys. Chem. Chem. Phys.* **20**, 27093 (2018)
- [3] I. Zhukov *et al.*, *J. Chem. Phys.* **155**, 224201 (2021)
- [4] D. Mims *et al.*, *Science*, **374**, 1470 (2021).

