

PL15-01

Silicon platform for applications to spin-based quantum computing

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Silicon (Si) is a promising platform for implementing qubits of electron (or hole) spins in quantum dots (QDs), on the grounds of a long intrinsic decoherence time ($>$ msec), a possible high temperature operation ($>$ K), and compatibility in device fabrication with industrial technologies. Supported by these features challenges have been made to implement two-qubit gates with fidelity above the fault tolerant threshold^[1-5], quantum error correction^[6] and scale-up of qubit devices all necessary conditions for implementing universal quantum computers. In this talk I will review recent progresses in these challenges and remaining issues.

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Animal Detected Magnetic Resonance

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Small migratory songbirds are extraordinary navigators. Weighing less than 50 g, they fly thousands of kilometres between their breeding and wintering grounds, alone and at night, ultimately with centimetre precision. To do this they use the sun and the stars, olfaction and landmarks, but they can also find their way using the direction of the Earth's magnetic field. Despite more than 50 years of research, the biophysical mechanism of this remarkable magnetic sense remains obscure. In this lecture, I will discuss the mechanistic insights available from behavioural studies of birds subjected to radiofrequency magnetic fields. Such findings arguably offer the most convincing evidence to date that the geomagnetic compass relies on the quantum spin dynamics of light-induced radical pairs in cryptochrome flavoproteins located in photoreceptor cells in the birds' eyes.

Funding: European Research Council, Synergy Grant, *QuantumBirds*, grant agreement 810002, under the European Union's Horizon 2020 research and innovation programme.

Tightly Bound Radical Pairs: Sensitivity to weak magnetic fields where it ought not to be

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The Radical Pair Mechanism (RPM) accounts for the magnetic field sensitivity of a large class of chemical reactions and is hypothesized to underpin numerous magnetosensitive traits in biology, including the avian compass sense [1,2]. A tenet of the RPM is that sensitivity to weak magnetic fields is acquired from coherent spin dynamics of well-separated, weakly coupled electrons. Radical pairs in close contact, with strong inter-radical coupling, were generally believed to be insensitive to weak applied magnetic fields due to arrested spin dynamics. This led - and still leads - to the perception that for mobile radicals separation of the radicals to distances for which exchange and electron-electron dipolar interactions have decayed to a level comparable to hyperfine interactions and subsequent reencounter(s) are essential [1]; for immobilized radical pairs, such as radical pairs in cryptochrome and other protein bound radical pairs, an electron transfer chain is generally deemed vital for permitting weak-field sensitivity [2].

Here, I will demonstrate that this dogma does not necessarily hold. Specifically, I will argue that, unexpectedly, radical pair systems can be sensitive to Earth-strength magnetic fields even if the radical partners are in contact, provided that the recombination reaction is strongly asymmetric, thereby invoking the quantum Zeno effect [3,4]. I will analyze the nature and potential of this effect in several contexts. First, I will discuss the infamous FAD-superoxide radical pair bound in the avian magneto-sensory protein cryptochrome, for which magnetosensitivity has been postulated and rejected based on the argument of excessively fast spin relaxation and strong inter-radical coupling [6,7]. Using molecular dynamics-informed spin dynamics calculations, I will show ample magnetosensitivity that is resilient to fluctuations in inter-radical interactions and persists across realistic scenarios with many hyperfine-coupled nuclei and with spin rotational relaxation, thereby providing a credible explanation for low magnetic field effects of tightly bound superoxide in biology. Second, I will explore magnetic field effects in lipid peroxidation, where the slow diffusional dynamics in the lipid membrane likewise give rise to conditions widely viewed unsuitable to support effects due to weak magnetic fields [8]. Exploring realistic dynamical scenarios including spin relaxation through Brownian dynamics and the stochastic Schrödinger equation, here too unexpected magnetosensitivity will emerge.

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IL16-03

Theoretical insights on radical pair dynamics in biological magnetoreceptors

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The laws of physics, both classical and quantum, are fundamental to the functioning of living organisms. As a physicist, I recognize that many biological characteristics are rooted in the principles of classical physics, often taught in introductory courses. However, several critical biological processes are governed by quantum physics, particularly those involving the transitions of electrons between states. This quantum behaviour is evident in all chemical transformations, such as the optical transitions induced by light absorption in biomolecules.

In this talk, I will explore a compelling example of quantum behaviour in biology, as it comes in animal navigation. Recent experimental findings suggest that migratory songbirds can detect the Earth's magnetic field through the quantum spin dynamics of light-induced radical pairs in cryptochrome proteins in their retinas^[1,2]. I will review these findings and provide a theoretical interpretation, discussing various models developed to describe the underlying spin dynamics in complex biological systems quantitatively.

Specifically, I will introduce the concept of the chemical compass^[3] and detail the elementary reaction steps involved. The focus will then shift to cryptochrome's activation and deactivation processes, examining the protein's magnetic sensitivity within the context of the protein-cofactor system^[1,4,5]. A significant portion of the lecture will address the dynamic nature of proteins, influenced by thermal fluctuations, and how this motion affects the sensitivity of the chemical compass. Proteins are not static; their thermal fluctuations induce spin relaxation in radical pairs formed within them. Upon generation, a radical pair enters an entangled quantum state, such as a single state, characterized by substantial coherence between the electrons, indicating their interdependence within the same physical entity. I will present molecular dynamics simulation results, utilizing three-dimensional protein structures to investigate these thermal motions^[1,4-6].

Additionally, I will discuss various theoretical approaches, including Redfield theory^[7] and the stochastic Schrödinger equation^[8], to describe how fluctuating interactions impact the coherence of spin states within the protein system using modern computational platforms^[9]. The presentation will conclude with a discussion on spin dynamics and spin relaxation in other biological systems beyond avian magnetoreception, highlighting the broader implications of possible quantum effects in biology.

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Electron Spins at Work in Organic Radical Batteries

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Batteries with polymer electrode materials containing stable radicals are promising alternatives to conventional lithium-ion batteries. However, the performance of organic radical batteries (ORBs) lags behind their lithium-containing counterparts. A further improvement of ORB technology requires an in-depth understanding of the charging and discharging processes on the molecular level. Electron spins can serve as local probes for elucidating redox reactions associated with the operation of ORBs. EPR spectroscopy can thus be employed to study charging and discharging processes in this promising class of electrochemical power sources.

In this presentation we report on the development of a versatile on-substrate electrode setup for spectro-electrochemical 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^[2] as active electrode material demonstrate a strong decrease in the number of paramagnetic centres upon oxidising the film. 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 pulsed EPR measurements on ORB electrode materials in various states of charge indicate the formation of electrochemically inactive islands. By simulating the spectral distortion caused by instantaneous diffusion, we obtain information on the local spin concentration in these islands, which complements the information on the ‘bulk’ spin concentration determined by quantitative continuous-wave EPR spectroscopy.^[3]

We will further report on our recent efforts towards developing cost-effective and accessible electrochemical cells for automated quantitative in-operando EPR experiments as well as electrochemical measurements.

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Probing the Non-Perturbative Magnetic Resonance Drive Regime with Electron-Hole Spin-Pairs in a π -Conjugated Polymer

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Spin-dependent charge carrier recombination currents in π -conjugated polymers are governed by radical pair physics, reflecting the spin-permutation symmetry of electron-hole spin-pair states. This effect has been extensively utilized in the past to detect magnetic resonance under conditions where conventional inductively detected magnetic resonance spectroscopy fails. These conditions include low spin polarization, such as low static magnetic fields, room temperature, and thus, typical electronic device operating conditions, or low-dimensional systems such as thin-film systems containing small spin ensembles [1].

Over the past decade, there has been an increasing body of theoretical [2-3] and experimental [3-6] work showing this mechanism can also be utilized to study the strong-drive, non-perturbative magnetic resonance regime, in which the amplitude of the magnetic resonant radiation is comparable to the static Zeeman field, changing the quantization axis and causing the emergence of spin-light hybrid states [2]. This results in a variety of electrically detectable non-linear magnetic resonance behaviors, such as spin-collectivity (i.e., the spin-Dicke effect) [2,4], multi-photon magnetic resonance [3,5,6], and fractional g-factor transitions [3]. Figure 1 gives an overview plot representing the results of Floquet theory-based numerical calculations for a bipolar injection device (i.e., an organic light-emitting diode) based on a fully deuterated MEH-PPV thin film. This presentation focuses on recent progress in experimentally confirming some of these phenomena [6]. These include monochromatic two- and three-photon electron spin transitions, as well as their non-Bloch Siegert-type shifts with increasing drive amplitude. Additionally, it discusses the non-trivial dependence on the angle between the drive fields and the static Zeeman field, and the implications of the hybrid light/matter states whose existence this work has confirmed for developing high-fidelity sensing qubits with long coherence times.

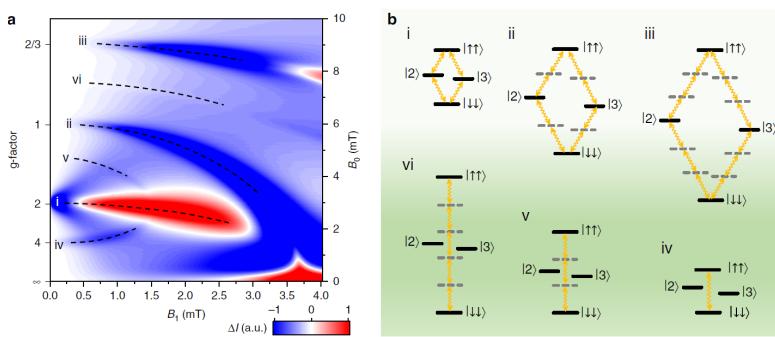


Figure 1. (Adapted from Ref. [3]). (a) Overview plot showing a variety of spin-dependent recombination current changes in a deuterated MEH-PPV device under 85 MHz RF excitation, as a function of drive field amplitude B_1 and the static field B_0 . (b) Illustration of the physical mechanisms corresponding to the different current change domains in (a).

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Spin dynamics in singlet fission

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Singlet fission is a multiexcitonic process that has potential applications in areas ranging from solar energy conversion to medical imaging. Spin is central to the singlet fission process. Although the singlet starting point and triplet end point of this process were considered obvious to the community, a series of experiments in 2017^[1,2,3] demonstrated that higher multiplicity spin systems (particularly spin quintets) played a critical role in the dynamics of singlet fission. Since then, a large number of studies have explored the increasingly rich spin ecosystem that emerges from this seemingly simple process.

In this talk, we will present a series of investigations into the nature, dynamics and coherence of spins resulting from singlet fission. The studies discussed will be primarily based in acene dimers, a model system for exploring and controlling singlet fission.

Experimentally, we will present new techniques for identifying and measuring the dynamics of spin based on the PEANUT electron spin resonance sequence^[4]. We will also show that coherent and incoherent approaches yield inequivalent results, indicating the presence of different spin populations.

Theoretically, we will explore the underlying mechanisms which drive spin dynamics^[3], and discuss approaches for experimentally discriminating these models using magnetically oriented measurements.

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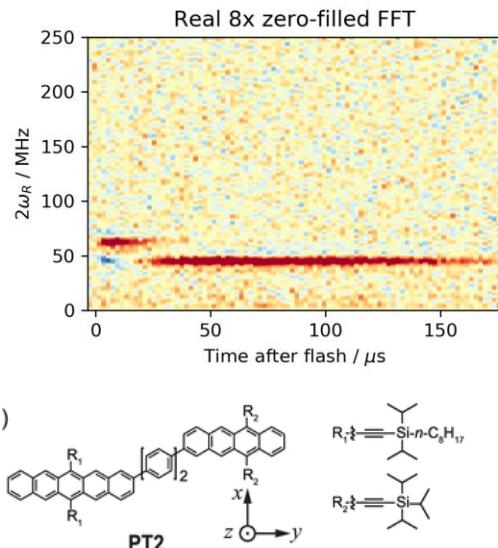


Figure 1. Fourier deconvolution of an electron spin resonance (ESR) PEANUT measurement of a tetracene-pentacene heterodimer following photoexcitation. The contribution of spins with different multiplicities can be clearly identified.

IL16-07

Exciton and spin dynamics of luminescent molecular materials

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The spin of ground and excited levels in molecular materials dictate the exciton mechanisms for any photonic, optoelectronic and quantum technology applications. This talk explores the photo- and spin physics of excitons as revealed by optical and magnetic resonance studies. Studies of spin conversion and the orbital-nature of the triplet excitons that underpin luminescence are presented for novel series of fluorescent and phosphorescent emitters. Recent interest in organic radicals containing unpaired electrons has emerged from the design of new materials that undergo efficient light absorption and emission from transitions between doublet spin ($S = 1/2$) ground and excited levels. As well as being potential candidates for functional emitters in light-emitting devices, opportunities emerge to couple their optical, spin and magnetic properties in molecular excitons that could enable future quantum and photonic technologies.

Quintet and Triplet Generation in Intramolecular Singlet Fission

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High-spin states are crucial in various organic applications, spanning from optoelectronics to quantum information and singlet fission (SF). This talk focuses on the generation of quintet and triplet states through intramolecular singlet fission (iSF). The principle is based on a photoexcited singlet exciton rapidly decaying into spin-correlated triplet pairs, forming singlet, triplet and quintet states, before dissociating into free triplets (Fig. 1). The investigation leverages the combination of the complementary techniques of optical spectroscopy, such as transient absorption (TA) and magnetic field dependent photoluminescence (magPL), with electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR), to monitor the intermediate states with different spin multiplicities. TA thereby probes the rapid decay of singlet excitons into spin-correlated triplet pairs and the detection of long-lived triplet states. Complementary, EPR spectroscopy allows identifying the involvement of exchange-coupled triplet pairs with quintet character, which dissociate into triplet excitons via the singlet fission process. MagPL and ODMR completes the picture by examining the high spin states participating in luminescence, providing a comprehensive understanding of all pathways.

We focus on novel concepts of intramolecular singlet fission based on units of the SF-active chromophore diphenylhexatriene (DPH). We found that upon fast iSF to generate strongly exchange-coupled triplet pairs, the efficiency of dissociation into free triplets strongly depends on the overall geometry and the number of molecular units. Notably, the involvement of the quintet states persists across all oligomers and can be detected in ODMR by spin dependent emission. By characterizing various oligomers, we investigate the dynamics of the involved spin states to establish a general framework for triplet and quintet generation in these systems.

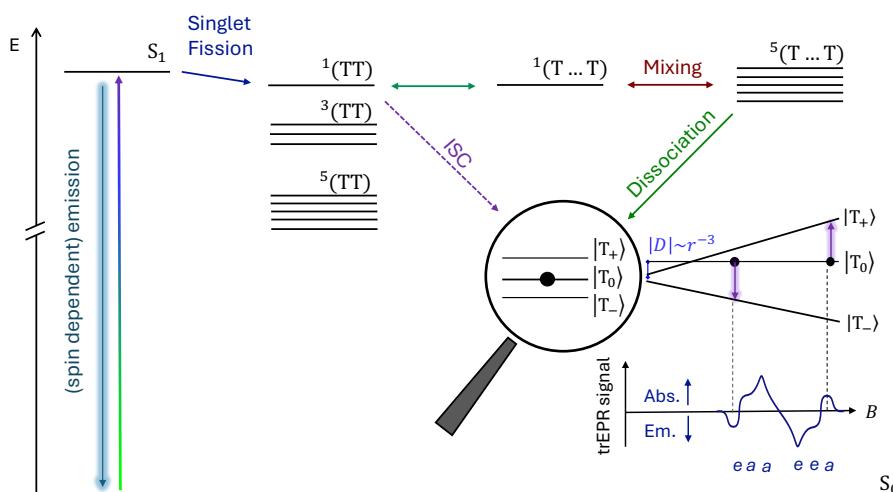


Figure 1. Spin-sensitive techniques monitor the involvement of different spin states in intramolecular singlet fission.

IL16-09

Mapping electron–chirality interactions by single-molecule junctions

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The interplay of electrons with a chiral medium has a diverse impact on science and technology, and particularly on electronic transport in chiral conductors ranging from bulk semiconductors down to individual molecules. However, understanding this interaction at the atomistic level is yet to be reached. Here, we use single-molecule junctions based on an individual helicene molecule suspended between two sharp metal electrodes as a testbed for such interactions. We find that the chiral single-molecule junctions behave as a combined magnetic-diode and spin-valve device. We identify the magnetic-diode behaviour with the Electrical Magneto-Chiral Anisotropy (EMCA) effect. In contrast, the spin-valve functionality is linked to the Chirality Induced Spin Selectivity (CISS) effect. These findings map the different interactions between electrons and a chiral medium at the atomic-scale, while the found atomic-scale coexistence of the EMCA and CISS effects can advance spintronics by achieving combined spintronics actions in a single device.

Detecting Chirality Induced Spin Selectivity using Photodriven Electron Spin State Teleportation

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Recently, we demonstrated that the chirality-induced spin selectivity (CISS) effect strongly influences the spin dynamics of photodriven charge separation in isolated covalent donor-chiral bridge-acceptor ($D-B\chi-A$) molecules.¹ Through the use of time-resolved electron paramagnetic resonance spectroscopy we showed that charge separation through a chiral bridge introduces triplet character into the initial spin state of the radical pair compared to an achiral bridge, which is purely singlet. Although this effect is attributed to CISS, the specific mechanism of this process remains an open question. One route to further explore the mechanism of CISS in photodriven electron transfer processes is through the application of a quantum teleportation protocol.²

We have also demonstrated electron spin state teleportation in a covalent organic donor-acceptor-stable radical ($D-A-R^\bullet$) system.³ Following preparation of a specific spin state on R^\bullet in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair $D^{\bullet+}-A^{\bullet-}$. The Bell state measurement step is the ultrafast chemical reaction: $D^{\bullet+}-A^{\bullet-}-R^\bullet \rightarrow D^{\bullet+}-A-R^\bullet$. Quantum state tomography of the R^\bullet and $A^{\bullet+}$ spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R^\bullet is teleported to $D^{\bullet+}$ with high fidelity. This protocol for quantum teleportation requires entanglement between, $D^{\bullet+}-A^{\bullet-}$, without which quantum state transfer is not possible; in addition, the phase of the teleported spin state is particularly sensitive to the Bell state of $D^{\bullet+}-A^{\bullet-}$. Both of these factors can be used to more thoroughly characterize the spin state produced through CISS.

Using an organic acceptor-chiral bridge-radical ($A-B\chi-R^\bullet$) molecule, and a magnetically equivalent achiral reference, we explore quantum state teleportation via hole transfer and the effect that a chiral bridge has on the fidelity of teleportation.

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Optimising the spin coherence properties of photogenerated quartet states

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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 optoelectronic and quantum sensing devices.^[1] Typically, they consist of an organic chromophore covalently attached to a stable radical as shown schematically in Fig. 1. Upon photoexcitation, the chromophore triplet state is rapidly generated by a process referred to as radical-enhanced intersystem crossing. If the exchange coupling J_{TR} between the chromophore triplet state (T) and the radical (R) spin centres is strong, compared to other magnetic interactions active in the system, quartet states may be formed by spin mixing.

For any applications of such photogenerated high-spin systems in molecular spintronic devices, their optical and magnetic properties are of major interest. In this contribution, we present our recent work focused at exploring how to control the properties of photogenerated quartet states, in particular their spin coherence times, and illustrate that the latter can be optimised by rational design.^[2-6]

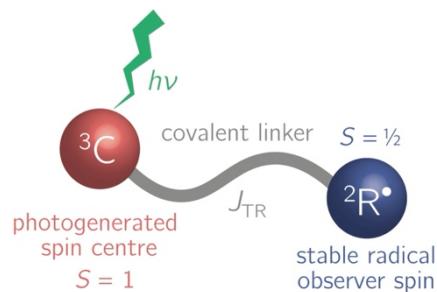


Figure 1. Schematic illustration of a photogenerated triplet–radical system.

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IL16-12

Nitrogen–Vacancy Centers in Diamond to Probe Photogenerated Radical Pairs

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Quantum sensing with the nitrogen–vacancy (NV) center in diamond provides a route for nanoscale NMR and EPR spectroscopies at the single- to few-molecule regime. Combined stabilization of shallow NVs and surface functionalization with molecules of interest enables chemical sensing with high sensitivity and nanoscale localization under ambient conditions.^[1,2] In particular, the use of NVs has been proposed to investigate photogenerated radical pairs (RPs) in proximal molecules by tracking charge separation and recombination, spin dynamics, and most recently, spin polarization attributed to chirality-induced spin selectivity (CISS). The use of NVs could provide insight into the spin dynamics involved in RP generation and spin evolution in systems ranging from biologically relevant proteins to molecular qubits for quantum information. Still, challenges remain to realize the use of NVs to probe photochemical reactions and RP species.

In this talk, I will motivate how single NV centers can be used to measure enantioselective spin polarization of photogenerated RPs in donor–bridge–acceptor molecules that may arise due to CISS. Our proposed quantum sensing scheme addresses how electron spin–spin dipolar coupling within the RP may inhibit sensing with a weakly coupled spin sensor, and leverages Lee–Goldburg decoupling to preserve the initial spin polarization for detection.^[3] I will then describe our experimental characterization of NV center charge-state stability and spin initialization fidelity under exposure to blue and UV irradiation, which would be necessary for RP generation in molecular samples.^[4] We find that these short wavelengths of light lead to reduced charge stability and spin contrast, and accelerated aging of the defect’s electronic environment. Despite this destabilization, we identify an experimental parameter space to maintain maximum sensitivity of the NV center for both blue and UV laser excitation and outline design rules for future sensing schemes.

This work is supported by the Swiss National Science Foundation Ambizione Grant PZ00P2_201590.

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IL16-13

ESR and SAXS studies on magnetosensitive protein reactions

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Many varieties of animals can sense the geomagnetic field and use it as a compass. Two hypotheses for the magnetoreception mechanism have been suggested. One is the magnetite model, where an iron oxide crystal (magnetite) senses the magnetic field. The other model is the chemical compass model, which involves the influence of a magnetic field on spin-dependent radical pair reactions. The radical pair in the cryptochrome is a primary candidate for magnetoreception in migratory birds. Radical pairs can be generated even when small molecules, such as drugs, bind to the abundant plasma protein, albumin. The albumin and 2,6-anthraquinone show a low-magnetic field effect on electron transfer reactions. An iron-sulfur cluster assembly protein (ISCA1), which has been suggested as a partner of cryptochrome, is a novel type of protein that responds to the magnetic field through self-aggregation reactions.¹ Iron-sulfur clusters of ISCA1s may contribute to this magnetic field effect. The discovery of these magnetically responsive proteins opens the possibility of controlling biological reactions by external magnetic fields or electromagnetic waves. The relationship between the magnetic structure of electron spins in these proteins and their three-dimensional structure is crucial for inducing magnetic effects. In this presentation, we will report on the latest studies of these proteins using electron spin resonance (ESR) and small-angle X-ray scattering (SAXS).

To identify the magnetic properties of radical pairs in albumin with 2,6-anthraquinone-disulfonate and flavin mononucleotide, we conducted time-resolved ESR. Several TRESR signals arising from radical pairs were observed and characterized through simulations. Exchange couplings and distances of radical pairs were determined, and the spin mixing mechanism related to the geometric structures was discussed.

ISCA1 has iron-sulfur clusters, either [2Fe-2S] or [3Fe-4S], and mononuclear iron². The magnetic properties of ISCA1 depend on which of these clusters are formed. We prepared the ISCA1s with only mononuclear iron (Fe-ISCA1s) from humans, pigeons, and European robins. EPR spectra showed the mononuclear iron signal at $g = 4.3$ while the Fe-S cluster signal at $g = 2$ was missing. SAXS revealed that these ISCA1s show field-dependent oligomerization/dissociation reactions. The field responsiveness of ISCA1s is conserved among species, but the structure of the oligomers and reactions differed. The findings suggest that mononuclear iron plays an important role in the field effect of ISCA1s.

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Multi-spin photoexcited state and unique DEP observed in anthracene-radical linked systems with extended π -conjugated spin coupler

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Potential use of multi-spin photoexcited systems and related spin systems has been expanded to modern technological applications.^[1,2] Understanding of the excited-state dynamics of the organic π -radical is crucially important, which is strongly related to the π -topology (π -conjugation network), radical induced enhanced intersystem crossing (EISC), and quantum-mixed states.^[1] We have reported the multi-spin quartet and quintet photoexcited states of π -radicals and their spin dynamics since 2000,^[3] and clarified the relationship between the spin-alignment and π -topology.^[3,4,1] In this presentation, after a short introduction of our previous studies of multi-spin photoexcited π -radicals, we report the spin dynamics and the dynamic electron polarization (DEP) generation of anthracene-radical linked multi-spin systems with extended π -conjugated linker (**2**, **3**). The DEP generation in the photo-excited states and its transfer to the ground-state are important for the application to the high-sensitive MRI or information science.^[5] Fig.1 shows a comparison between the TRESR spectra of **2** and **3** and that of the original verdazyl radical (**1**).^[6] According to become the expected J coupling weaker, the central peak intensity increases. Z peak intervals are a little change, although XY peak intervals decrease. Pulse ESR and transient absorption (TA) measurements were also carried out at 90 K using PMMA matrix. Spectral simulation taking the spin dynamics into account has almost revealed the DEP generation. The excited-state spin dynamics and the DEP generation mechanism, which is induced by the dipolar mixing between the quartet and doublet states, DEP generation in the multi-spin photoexcited states and its spin-selective transfer to the ground state, will be discussed based on the simulation approach of the TRESR spectra with the help of pulse-ESR and TA data.

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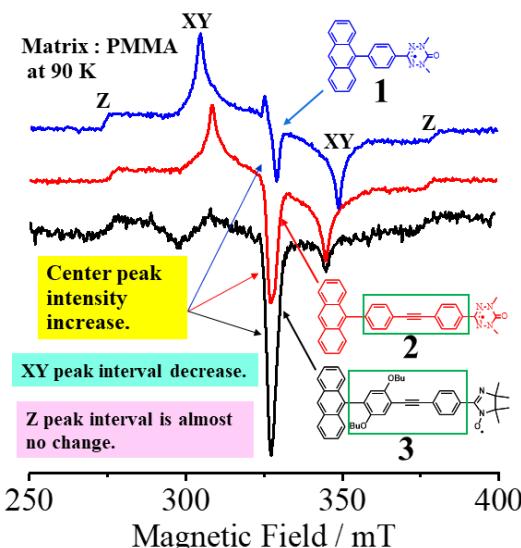


Figure 1. Molecular Structures and typical TRESR spectra of photo-excited multi-spin systems studied here.

Photogenerated Molecular Spin Qubits, Spin Polarization, and Relaxation

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Abstract: Radical elaborated spin-bearing Pt Donor-Acceptor and Donor-Bridge-Acceptor ligand-to-ligand charge transfer complexes have been used to control spin-dependent ground and excited state processes that include non-radiative lifetimes,^[1] magnetooptical activity,^[2] and ground state electron spin polarization.^[3,4] These molecules represent a new class of chromophore that can be photoexcited with visible light to produce an initial exchange-coupled, multi-spin, open-shell excited state. Following photoexcitation, the excited state rapidly decays to the ground state by magnetic exchange-mediated enhanced intersystem crossing (internal conversion). This process also generates excited state spin polarization and ground state electron spin polarization of the pendent radicals to enable synthetic control over the sign, magnitude, and nature of the spin polarization. Here we discuss our recent efforts using synthetic design principles to create new molecules that promote long-range electronic coupling and electron correlation,^[2,5] and the development of new platforms for spin control of excited state processes.^[1-4] We also present results that test theoretical hypotheses as they relate to how excited state pairwise superexchange interactions and energy transfer processes control the optical generation and manipulation of molecular spin qubits,^[3,4,6-8] and ground state spin relaxation processes in biradical systems.

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Towards Quantum Dynamic Therapy – Concept and Strategy of Radical-Pair Based Drug Delivery System –

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Drug delivery system (DDS) is based on nanocapsules having ~100 nm diameter, which are easily imported to cells by endocytosis. As a successful example of DDS, the lipid nanoparticle for mRNA vaccines involves ionizable lipids, which are protonated in response to the low pH in the endosome. The ionization leads to breakup of the endosome and mRNA release to the intracellular fluid. Photocontrol of the pharmaceutical activity such as photodynamic therapy is another type of advanced medical technologies, which markedly reduces side effects of pharmaceutics. The combination of these technologies, photo-triggered DDS, is center of focus^[1], but photon-based technologies are limited to the body surface since the light is absorbed/scattered by body tissues.

We propose a future medical technology named quantum dynamic therapy (QDT), which enables precise three-dimensional control of the drug release from a nanocapsule. QDT is based on magnetic field effects (MFEs) on the radical pair as shown in Fig. 1. Charge-neutral donor (D) and acceptor (A) molecules are embedded in the shell of a nonionic vesicle capsule, and hydrophilic pharmaceutical molecules (P) are encapsulated in the water pool of the capsule. Radical ion pairs are created by photoirradiation, which increases the charge density of the shell and expectedly induces disassembly of the capsule. The recombination lifetime of the radical ion pairs can be controlled by applied magnetic field or resonant microwave, so that the release efficiency of P should also be controlled magnetically. MFE is spatially modulated under a strong field gradient, which enables three-dimensional control of the release efficiency. Further, CIDEP/CIDNP due to the radical pair can be monitored by EPR/NMR imaging, which enables visualization of drug release.

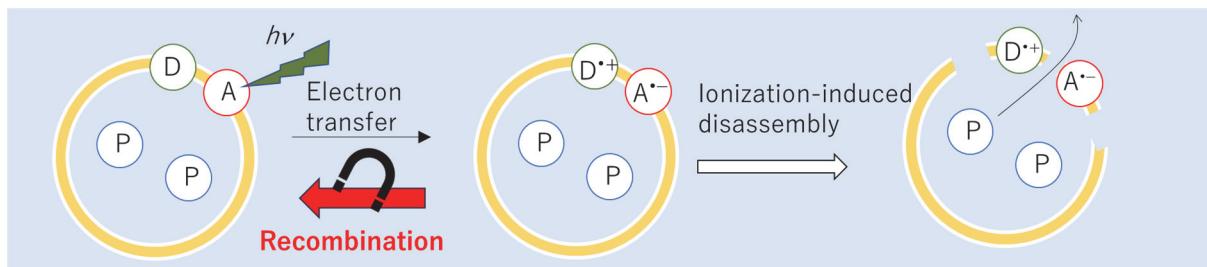


Figure 1. Conceptual scheme of nanocapsule for QDT.

For the above purpose, singlet-born radical pairs are ideal since the lifetime becomes longest at zero magnetic field or resonant field, which can be locally created with field gradients. In the talk, we will discuss the strategy to tackle with this challenging project mainly from the theoretical aspect. Recent experimental data of MFEs on a nanocapsule-embedded singlet radical pair will also be briefly introduced.

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Controlling high-spin states in luminescent radicals

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Luminescent trityl-based organic radicals offer an exciting optoelectronic platform where electron spin plays a central role in the exciton dynamics. Photoluminescence within the doublet ($S = 1/2$) manifold can be efficient, but the role of any quartet ($S = 3/2$) states in intra- and intermolecular dynamics is crucial for device operation.

High-spin states in radicals can act both as a synthetically-tunable platform for microwave manipulations, and are required for understanding the intermolecular triplet harvesting process which enable efficiency increases in organic light emitting diodes.

Here we investigate excited states in a range of luminescent radical-based systems via ultrafast optical spectroscopy in tandem with light-induced transient and pulsed ESR.

We study internal conversion and intersystem crossing dynamics in TTM radical derivatives and shed light on their excited state energetic landscapes. Using a model organometallic:radical blend, we demonstrate that triplets can be harvested by radicals already at picosecond timescales.^[1]

In a blend of a TTM derivative with 800 nm emission and MADN host we observe reversible radical-triplet cycling.^[2] These dynamics are rationalised by the spin statistics of the intermolecular encounter pairs (Fig.1). OLEDs based on this active layer achieve record efficiencies, while the triplet shelving states may contribute to their reduced roll-off.

Building on our demonstration of light emission following quartet state generation,^[3] we report new structures which clarify the role of the charge transfer states in the luminescent high-spin mechanism. Finally, we present an alternative design architecture, using a family of organic chromophores unexplored thus far, which also achieves emission following quartet generation, tuned to a different spectral region. This enhances their scope for future applications, such as quantum sensing with read-out via luminescence at biological conditions.

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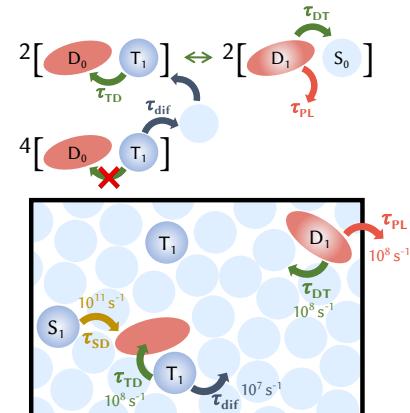


Figure 1. Intermolecular processes in the **MADN:TTM-TPA** blend, with optically measured rates.

High-contrast photoluminescence detected coherent spin manipulation in molecules at room temperature

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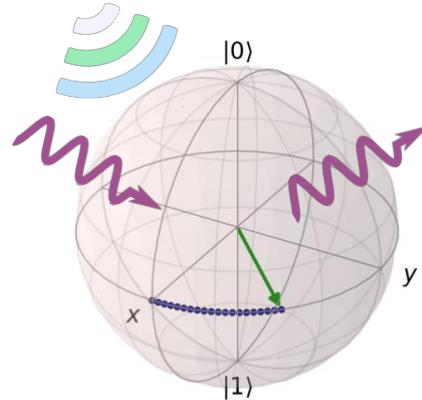
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Optically addressable spins are a promising platform for quantum sensing due to their ability to be readily prepared, coherently controlled, and sensitively read out. For example, solid-state defects with optically addressable spins have enabled remarkable demonstrations such as nanoscale magnetometry at room temperature. Complementary to solid-state defects, molecular systems are attractive for hosting optical-spin interfaces due to their chemical tunability and ability to be integrated with targets of interest. Such properties could be particularly beneficial for quantum sensing where, for example, precise spatial control between sensor and target is desirable. For quantum sensing, demonstrating the combination of room-temperature operation, coherent spin control, and high-contrast photoluminescence detected spin readout is desirable, combining sensitive detection capabilities with convenient operating conditions. Compared to solid-state defects however, such functionality has remained challenging in molecules. Here, using photoexcited triplets in organic chromophores as a model system, we demonstrate high-contrast photoluminescence detected coherent manipulation in both molecular crystals and thin films at room temperature^[1], and show how manipulation of multiple spin transitions can enhance the spin-optical dynamics of these systems. Overall, these results indicate opportunities for room-temperature quantum sensing with molecular spins.



Funding acknowledgment: this work was supported by UKRI [MR/W006928/1], EPSRC [EP/W027542/1, EP/F039948/1, EP/F04139X/1, EP/V048430/1], CDT-ACM [EP/S023259/1], Australian Research Council [CE170100026], and Sydney Quantum Academy.

*These authors contributed equally to this work: A. M., S. K. M., A. C.

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Modulation of Electronic and Exchange Coupling in Donor Acceptor Triads with Triptycene Bridges

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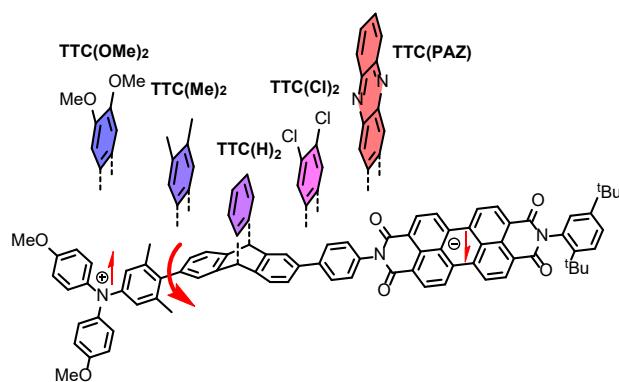
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Electron transfer (ET) coupling and exchange coupling are related by Anderson's perturbation theoretical approach. We developed molecular donor-acceptor triads where the bridge linking the triarylamine donor and the perylene diimide acceptor can be varied in a systematical way to tune orbital overlap and/or the local bridge state energy. In that way, we want to assess the influence of the bridge on the exchange and electron transfer coupling. As the bridge we used substituted triptycenes because their wings interact by homoconjugation which brings the kinetics of electron transfer in a time regime where it is sensitive to the spin exchange. Furthermore, triptycenes provide a stiff scaffold which reduces degrees of motional freedom between donor, bridge and acceptor. Thus, in one set of donor-acceptor triads we tuned the orbital overlap, that is, the dihedral angle between the individual building blocks by attaching methyl substituents to the phenylene rings linking the donor/acceptor to the triptycene. Investigation of the ET dynamics by magnetic field dependent transient absorption spectroscopy and modelling the resulting data set by quantum mechanical calculations based on the stochastic Liouville equation shows a clear correlation of the electronic couplings with the average cosine square of the dihedral angle. In the other set of triads, we modified the third wing of the triptycene by attaching electron donating or withdrawing substituents. Here we found a clear correlation of the electron transfer couplings and the exchange coupling with the inverse of the bridge state energy. The latter set of triads shows that triptycene is an ideal bridge as it allows electronic modification without changing structural parameters.



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High-field optically induced NMR hyperpolarization in solids

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Poor sensitivity is still one of the main barriers in cutting-edge applications of NMR spectroscopy for structural and chemical analysis. In this regard, hyperpolarization alleviates the sensitivity issue by enhancing the population imbalance between the nuclear spin states, and thus the NMR signal.

For solid-state NMR, optical hyperpolarization methods would be particularly enticing. They exploit transient electronic excited states as the polarization source, which can in principle induce very large nuclear spin polarizations. One such optical technique is solid-state photochemically induced DNP (photo-CIDNP), where light is used to excite a donor–acceptor system, generating a spin correlated radical pair whose evolution and decay build nuclear spin hyperpolarization. We recently demonstrated that bulk optical ¹H hyperpolarization can be obtained at 0.3 T by polarization relay from a synthetic donor–acceptor molecules.[1] Here, we extend the concept of ¹H and ¹³C photo-CIDNP from synthetic donor–acceptor molecules to the high magnetic fields required for high-resolution NMR spectroscopy, namely, 9.4 T and 21.1 T. [2,3]

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Tackling the problem of central spin decoherence

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Decoherence of a central spin in a quantum bath is important to quantum information science and technology involving spin qubits interacting with electron spins, nuclear spins or phonons in their environments. It is also relevant to understanding the dynamics of radical spins interacting with nuclear spins in chemical reactions and biological processes. Computing the central spin decoherence is in general hard due to the notorious complexity of quantum many-body problems. Here I will present a series of quantum many-body theory we developed in the past two decades to tackle the problem of central spin decoherence in quantum baths (such as interacting spin baths and boson baths). I will argue that for most cases, there exists a numerically efficient method for the central spin decoherence problem. I will discuss a few typical scenarios such as nuclear spin baths in solids, the spin star (Gaudin) model, and the spin-boson model. I will also discuss the dynamical decoupling control of central spin decoherence.

This work was supported by the Innovation Program for Quantum Science and Technology of China (Project 2023ZD0300600), the Hong Kong RGC General Research Fund (Project 14302121), the National Natural Science Foundation of China/Hong Kong RGC Collaborative Research Scheme (Project CRS-CUHK401/22), Hong Kong RGC Senior Research Fellow Scheme (Project SRFS2223-4S01), the Hong Kong Research Grants Council/Theme-based Research Scheme (Project T45-406/23-R), and the New Cornerstone Science Foundation.

Low-cost, high-throughput nuclear spin hyperpolarization and high resolution NMR relaxometry over ultra-wide magnetic field range

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The general theoretical approach for description of different types of spin hyperpolarization have been re-formulated in terms of level crossings (LC) and level anti-crossings (LAC) of interacting spin states^[1]. To explore fully the high potential of the unified approach by addressing to different types of LACs through magnetic field variation, a fully automatic low-cost field cycling add-on to cover the ultra-wide magnetic field range from 10 nT to 19.4 T was built in Novosibirsk^[2]. Our shuttling device is compact and compatible with any type of commercial high resolution NMR spectrometer. It allows high-throughput of para-hydrogen induced nuclear spin hyperpolarization (PHIP) and SABRE, as well as proton and heteronuclear photo-CIDNP and photo-SSABRE. We proved that the most efficient polarization transfer occurs at LACs and such transfer is of coherent nature. Based on magnetic field dependence, a facile experimental protocols were proposed for highly efficient hyperpolarization of ¹³C, ¹⁵N, ¹⁹F, ³¹P, ⁷⁷Se nuclei via adiabatic magnetic field modulation at LACs. Proposed approach makes it possible to improve the efficiency of hyperpolarization processes at zero and ultralow magnetic field (ZULF)^[3], as well as at weak and strong magnetic fields via application of shaped pulses of oscillating magnetic fields. For nuclear spins of molecular *para*-hydrogen interacting with catalytic complex we explored the *para*-*ortho* conversion rate dependence on magnetic field and found that energy level anti-crossing boosts conversion of *para*-hydrogen.

In spin chemistry, magnetic interactions of electrons and nuclei spin are encoded in field dependence of CIDNP that is modulated by nuclear relaxation dispersion. Theirs combined study over ultra-wide magnetic field range allows to disentangle contributions of the different mechanisms to singlet-triplet conversion and to reveal polarization transfer among nuclei. For set of well-designed of donor-acceptor dyads and flavin-adenine-dinucleotide (FAD)^[4] studied by ¹³C and ¹H field-dependent and time-resolved photo-CIDNP and supported by modern theoretical calculations we explained LACs in magnetic field dependence and determined the sign and the values of electronic exchange interaction in transient short-lived biradicals.

Funding: This work was supported by the Russian Science Foundation (grant number #23-73-10103)

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Towards Optical Overhauser DNP of biological systems

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NMR spectroscopy has long suffered from inherently low sensitivity which limits applications, not least in the case of volume-limited biological samples. While DNP methods seeking to enhance NMR sensitivity by microwave driven transfer of thermal electronic polarization to nuclei have been extensively investigated^[1], an attractive alternative is use of optical pumping to generate electronic hyperpolarization prior to electron-nuclear polarization transfer. The photo-CIDNP method based on the radical pair mechanism has been known since the late 1960s, but an underexplored route is hyperpolarization of electrons via the more recently discovered radical triplet pair mechanism (RTPM)^[2]. We have previously shown that continuous optical illumination of a high triplet yield dye and radical in solution can lead to ¹H NMR enhancements after Overhauser driven polarization transfer to solvent nuclei^[3]. 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 enhancement exceeds the Boltzmann limited value for microwave pumped Overhauser DNP.

While our initial work on Optical Overhauser DNP^[3-5] has focused on low magnetic fields (~0.35 T) as used in previous time-resolved EPR studies of the underpinning electron polarization mechanisms, for NMR applications a higher magnetic field will be required to provide increased chemical shift dispersion. With the expectation of diminishing electronic hyperpolarization and certainty of reduced Overhauser efficiency for dipolar transfer to ¹H at higher magnetic fields, we have developed a shuttle DNP approach based on a Magritek Spinsolve 43 MHz ¹H benchtop NMR system. Our system permits efficient optical polarization generation and transfer to nuclei at low-field within the magnet bore before rapid mechanical sample shuttling for detection of resolved ¹H NMR spectra at 1 T. Our recent results including preliminary optimization of the polarization field will be presented, alongside the first resolved spectra for hyperpolarized amino acid substrates. We will also highlight sensitivity of the RTPM to the effects of pH and ionic strength which were identified through our optical DNP studies of amino acid containing solutions. Finally we discuss the underexplored question of the magnetic field dependence of the RTPM generated electronic hyperpolarization.

We gratefully acknowledge financial support for this work from the Royal Society [IEC\R3\213064] and Royal Society of Chemistry [E21-3124554325]

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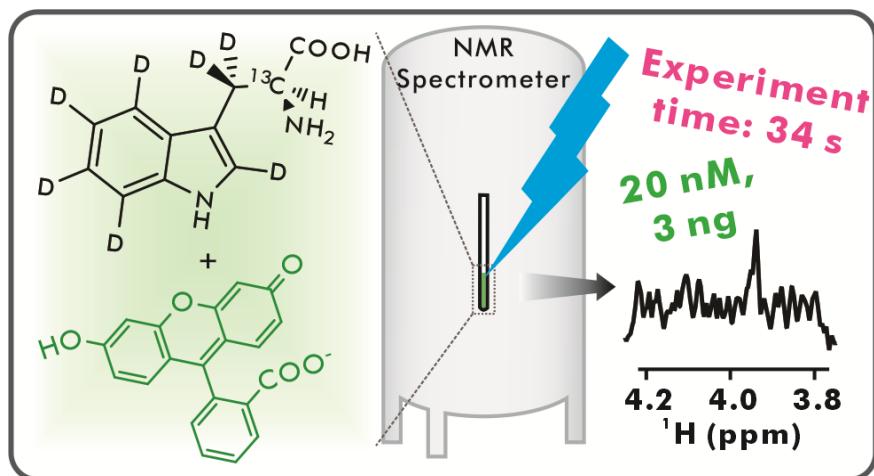
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LC-Photo-CIDNP: A New Avenue to Hypersensitive Data Collection in Biomolecular NMR

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Liquid-state low-concentration photochemically induced dynamic nuclear polarization (LC-photo-CIDNP) is an emerging technology tailored to enhance NMR sensitivity via LED-mediated optical irradiation. LC-photo-CIDNP enables the detection of solvent-exposed aromatic residues in isolation and within polypeptides and proteins (1-3). This presentation will focus on describing how amino-acid isotopologs bearing quasi-isolated spin pairs (QISP) lead to unprecedented nuclear-spin hyperpolarization of amino acids and proteins due to both dark (LED-off) and light (LED-on) effects (4). The magnetic-field dependence of LC-photo-CIDNP of biomolecule (within the high-field regime) is particularly interesting, and will be described in the context of low-field NMR and field cycling (1,3). Enhancement factors up to 1,200 were obtained at 50 MHz (1.18 T), suggesting exciting avenues to explore the early and late stages of protein folding and aggregation in physiologically relevant environments at high sensitivity.



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Materials chemist meets Photo-CIDNP

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Photochemically induced dynamic nuclear polarization (Photo-CIDNP) is a method to improve the sensitivity of NMR and MRI by light irradiation. Its major advantage over other DNP methods is that it does not require microwave irradiation. We believe that this feature will enable DNP in living cells and animals in addition to DNP of biomolecules in action.

Numerous excellent Photo-CIDNP studies have been performed to date, providing deep understandings of the spin-polarization generation mechanism and new understandings of biomolecular behavior. Building on these many accomplishments, we believe that the possibilities of Photo-CIDNP can be further expanded by integrating materials chemistry.

In this presentation, we would like to report the progress of our new challenge on Photo-CIDNP. For example, many of the dyes used in Photo-CIDNP have short wavelength absorption and insufficient stability. Therefore, we are developing more stable dyes that can absorb longer wavelengths of light by utilizing our experience in the field of photochemistry. In addition, we are also screening candidate quenchers to find many new combinations of dyes and quenchers. Furthermore, by developing quenchers that respond to specific substrates, we propose the application of Photo-CIDNP for monitoring enzymatic reactions.

IL17-08

Progress report on the solid-state photo-CIDNP effect and its application as photo-CIDNP MAS NMR in the Leipzig group

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The Leipzig group has delved into the captivating realm of the solid-state photo-CIDNP effect, pushing the boundaries of its application in photo-CIDNP MAS NMR. The work has particularly focused on:

(i) The donor cofactor Photosystem I and its functional symmetry [1]; (ii) The electronic structure of the cofactors of photosynthetic reaction centers (RCs) heliobacteria and their dynamics [2,3]; (iii) flavoproteins (LOV domains) showing a solid-state photo-CIDNP effect for ¹H, ¹³C and ¹⁵N, demonstrating efficient spread of ¹H hyperpolarization to bulk proton pool of protein and solvent, allowing for distance dependent experiments [4,5]; (iv) to observe and discuss unexpected ¹⁵N signals in shuttle-MAS NMR in RCs and LOV domains [6]; (v) implementation of LOV domains into trehalose matrix to stabilize spin-correlated radical pairs as well as radicals and the analysis of these species by experimental and theoretical means [7,8]; (vi) Furthermore, reviews have been published on Photo-CIDNP MAS NMR as method for structural elucidation [10], on the spin-dynamics of flavoproteins [11] and on the entire field of hyperpolarized magnetic resonance [12].

Finally, we would like to acknowledge that the rise of the DFG-founded network HYP*MOL, aiming for the intellectual unification of magnetic resonance, spin-chemistry and molecular spintronics, opens for new directions of research.

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Quantum diamond sensors for biological research

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The negatively charged nitrogen-vacancy center (NV^- , Figure 1) is a versatile tool for sensing a wide range of physical and even chemical parameters at the nanoscale. The single NV center can be optically measured, and among solid-state electron spins, it has the longest spin coherence times at ambient conditions [1]. The NV^- is therefore attracting interest as the smallest quantum sensor in biological research.

Detonation nanodiamond (DND) is the smallest class of diamond nanocrystal capable of hosting various color centers with a size akin to molecular pores. Nonetheless, recent NV^- enhancement in DND has yet to yield sufficient fluorescence per particle, leading to efforts to incorporate other group-IV color centers, such as silicon-vacancy centers (SiV^-), into DND^[2,3].

In this presentation, we mainly report on efficient observation of the characteristic optically detected magnetic resonance (ODMR) NV^- signal in silicon-doped DND (Si-DND) subjected to boiling acid surface cleaning.^[4] The NV^- concentration is estimated by electron spin resonance spectroscopy to be 0.35 ppm without any NV^- enrichment process. A temperature sensitivity of $0.36 \text{ K}/\sqrt{\text{Hz}}$ in an NV^- ensemble inside an aggregate of Si-DND is achieved via ODMR-based technique. A comprehensive transmission electron microscopy survey reveals that the Si-DNDs core sizes are $\sim 11.2 \text{ nm}$, which is the smallest nanodiamond ever reported among the nanodiamond's temperature sensitivity studies. Further, temperature sensing using both SiV^- (all-optical technique) and NV^- (ODMR-based technique) in the same confocal volume is demonstrated, showing Si-DND's multimodal temperature sensing capability. The results of the study thereby pave a path for multi-color and multimodal biosensors and for decoupling the detected electrical field and temperature effects on the NV^- center.

The authors are grateful for financial support from the MEXT-QLEAP Project (No. JPMXS0120330644) and, partially from CREST (No. JPMJCR23I5) and partially from the Collaborative Research Program of ICR, Kyoto University (No. 2024-71, 75, 76, 77, 80).

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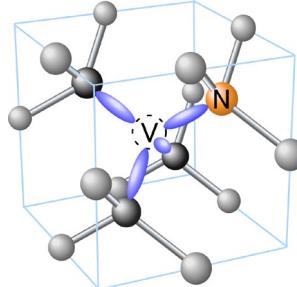


Figure 1, The NV center in diamond.

Label-free Quantification of Cell Function using Quantum Sensors in Nanostructures

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Recent advancements in nanoscale quantum sensors, capable of optical detection at ambient conditions, have significantly advanced quantum technologies for biochemical detection within biological engineering. Particularly, enzyme-linked immunosorbent assays (ELISA) utilizing quantum technology have achieved a detection limit as low as $82 \times 10^{-21} M$ in a biotin-avidin model system^[1]. Additionally, in-cell measurements of biochemical parameters such as temperature^[2] and radicals^[3] are expanding the capabilities of quantum life sciences^[4]. The primary advantage of utilizing quantum measurement in the detection of biochemical environments is its capability for high-precision quantification. Notable achievements include temperature detection with an accuracy below 0.1 degrees and nuclear magnetic resonance (NMR) measurements with a spatial resolution under 1 nanometer^[5, 6]. These innovations highlight the transformative potential of quantum sensors in significantly improving the precision and range of biochemical measurements at the intracellular level.

In this presentation, I will discuss a novel quantum sensing modality using diamond pillars equipped with single nitrogen-vacancy (NV) centers to measure cellular activities, such as the generation of radical molecules and cell differentiation. Positioned just 10 nm from the surface, these NV centers are embedded within each diamond pillar, which also serves as an optical cavity to enhance photon collection. This nanostructured quantum sensor design has been optimized to minimize cellular damage while maximizing sensitivity for in-cell quantum measurements.

Figure 1 presents the results of Double Electron Electron Resonance (DEER) measurements, utilizing Nitrogen-Vacancy (NV) centers on the surface of diamond pillars to measure surface electron spins. This advanced quantum sensing technique demonstrates potential for sensitivity enhancement through entanglement in such quantum structures. In this presentation, I will introduce new results on the detection of intracellular parameters using nanostructures, and discuss a novel bioengineering approach that combines optical tweezers with nanostructures for enhanced cellular analysis.

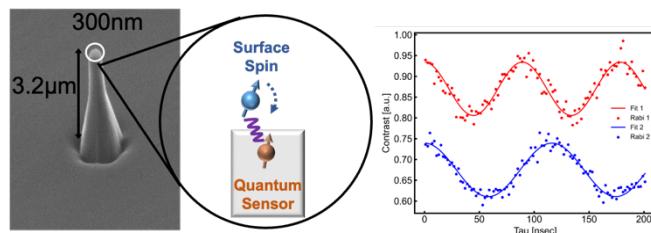


Figure 1. Double Electron Electron Resonance (DEER) measurements of Surface Electron spin using NV center on surface of diamond pillars.

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Nanoscale Quantum Sensors for Life Science

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Fluorescence microscopy is an essential tool in modern life sciences, enabling the observation of intracellular calcium ion dynamics in small animal brains, tracking single biomolecules in living cells, and super-resolution imaging of nanoscale cellular structures and molecular processes. However, despite the development of various fluorescence probes, measuring physical and chemical parameters, such as temperature and pH, within microenvironments remains challenging. This difficulty in quantitative measurement at the microscopic level hinders the full quantification of intracellular phenomena.

Recently, nanoscale quantum sensors using nanodiamond NV centers have garnered attention for their potential to measure these microenvironments quantitatively. The NV centers contain triplet electron spins, and their fluorescence intensity depends on the probability amplitude of the spins. Consequently, these nanoscale quantum sensors can measure various physical and chemical changes that influence the spins, allowing the measurement of parameters under fluorescence microscopy. The sensors are exceptionally small, miniaturized to as tiny as 5 nm,¹ and can be easily chemically modified using surface carboxyl groups, enabling straightforward bioconjugation.² This advancement allows the delivery of nanoscale quantum sensors to target sites within cells and the quantitative measurement of various parameters of the surrounding microenvironment under fluorescence microscopy. Initially, nanoscale quantum sensors could only measure magnetic fields, electric fields, and temperature. However, we have expanded their capabilities to include the measurement of pH, viscosity, molecular structural changes, radicals, and high-sensitivity detection of biomolecules.³⁻⁶

In this presentation, we will introduce our latest research on the application of nanoscale quantum sensors in life sciences. We will present experimental data highlighting their capabilities and discuss the potential and future prospects of these sensors in various fields of life science.

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Defect interplay for nuclear hyperpolarization in diamond

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In recent years, optically pumped electron spins of color centers in wide band gap materials have become an attractive way to produce hyperpolarized nuclear states and to study a variety of quantum mechanical effects [1,2,3]. We utilize a 10 MeV electron beam to tune the nitrogen vacancy (NV) center concentration in five diamond samples with similar initial substitutional nitrogen (P1) concentration. We observe inhomogeneous defect distributions regarding P1, NV and NVN defects by Fourier-transform infrared spectroscopy, electron paramagnetic resonance spectroscopy, confocal photoluminescence scans and polarized light microscopy. Furthermore, we perform field cycling NMR experiments to measure the bulk ^{13}C hyperpolarization of each sample (Fig. 1). We identify NV-P1 and NV-NV cross relaxation (CR) as polarization transfer process to nearby ^{13}C spins. Different dependencies for the hyperpolarization signal for NV-P1 and NV-NV CR were found. Therefore, we propose that inhomogeneities and the interplay between the defects therein are crucial for NV-driven nuclear hyperpolarization.

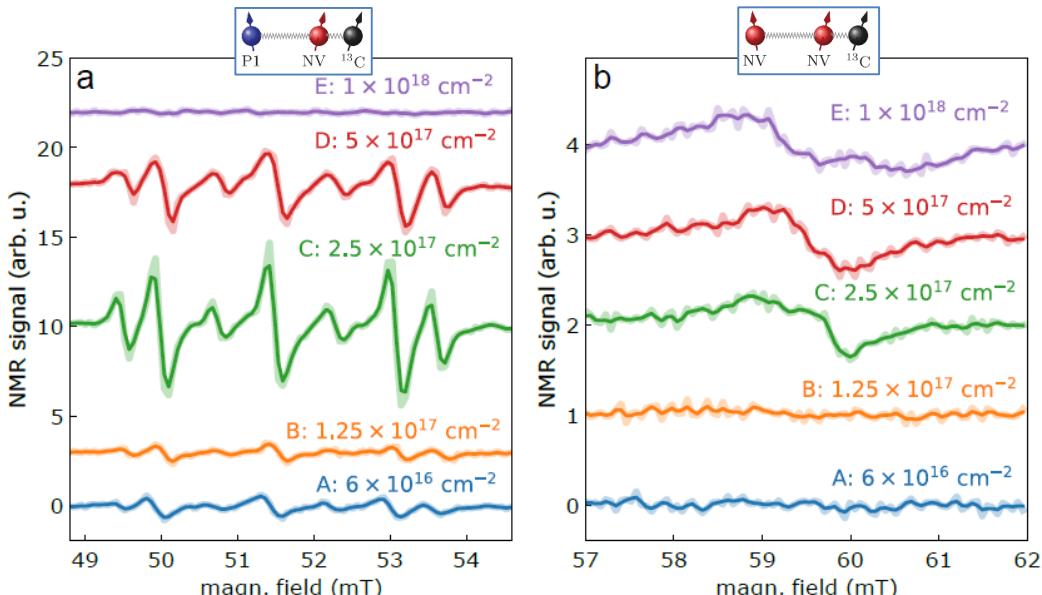


Figure 1. Field cycling nuclear hyperpolarization measurements for five different diamond samples. The x-axes show the low magnetic field during the laser illumination (520 nm, 12 s, 3 W) and the y-axes the corresponding ^{13}C NMR signal strength after sample transfer in the high field NMR probe. a) Characteristic pattern of NV-P1 cross relaxation (CR). b) Characteristic pattern of NV-NV CR.

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Large-scale Quantum Information Processing in Hyperpolarized Molecular Solids: Achievements and Prospects

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Entanglement is a unique resource for quantum information processing and computation. To explore the application of entanglement in various quantum information tasks, systems that exhibit large amounts of entanglement are required. Basically, such systems can be created in two ways. The first method is to increase the number of qubits in an entangled state. The second method is to increase the number of entangled states for a given number of qubits. Here, we combine both methods in a new pulsed magnetic resonance experiment capable of creating a large number of multi-qubit entangled states in molecular solids.

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 multi-qubit 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 ± 0.03 ^[1].

To assess the created quantum system, we determine the dimension of the entangled computational (Hilbert) space according to $\text{dim} = d^N$. Here d stands for the entangled dimensions and N is the number of involved qubits^[2]. 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 compares favorably with the dimensions achieved in recent quantum advantage experiments using superconducting qubits^[3,4] or photons^[5,6]. Since pure states with vanishingly small intrinsic error rates are initialized by our method, quantum error correction is of less importance and can be achieved with substantially less qubit overhead. Because of the nuclear hyperpolarization, created at LAC, high-dimensional multi-qubit entanglement can be realized at room temperature. We therefore expect that the LAC experiment developed in this work paves the way for large-scale quantum information processing with more than 10 000 multi-qubit entangled 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.

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From CIDEP to MASERS: A Dielectric Journey

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The spin of an electron allows detailed information about the magnetic interactions of an ensemble of unpaired electrons to be obtained via EPR spectroscopy.

Furthermore, spin systems may be prepared in a non-Boltzmann state, resulting in spectra showing enhanced absorption or emission, as originally – and unexpectedly – observed in NMR and ESR spectra following flash-photolysis, and given the acronyms: CIDNP and CIDEP, respectively. Non-Boltzmann spin populations (*usually*) increase the sensitivity of the experiment, and allow, for example, the use of direct detection, continuous-wave EPR without the use of magnetic field modulation, for example for the investigation of photo-generated species such as spin-correlated radical pairs and triplet states.

Another technological development that enhances the sensitivity of EPR spectroscopy is the use of dielectric resonators. A typical example is the use of Corundum, a crystalline form of Al₂O₃, commonly known as sapphire.

The use of both electron spin-polarization and dielectric resonators was fundamental for our realization of a solid-state, room-temperature, continuous-wave MASER, using NV-centers in diamond [1,2].

Acknowledgements

I am indebted to many coauthors, but particularly Jonathon Breeze, Enrico Salvadori and Christopher Zollitsch for long-standing, fruitful and above-all enjoyable collaborations.

Financial support from the EPSRC and Saarland University is gratefully acknowledged

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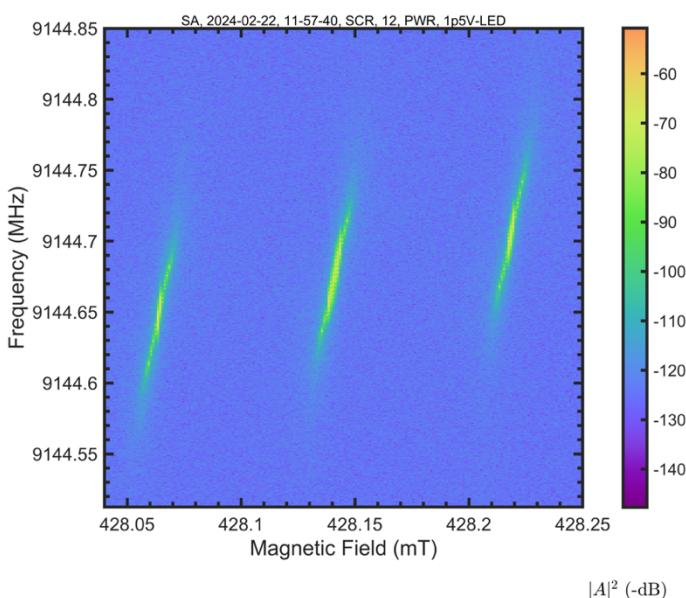


Figure 1: Illustration of the MASER output of a diamond containing NV-centers, under continuous-wave, 520 nm illumination, housed in a dielectric resonator, held in a copper cavity, placed in a Helmholtz-type electromagnet, at room temperature. Credit: Dr. Christoph Zollitsch (UCL and Saarland University)

Large dynamic electron polarisation generated in the quenching of triplet Xanthene dyes by nitroxide radical

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Photoinduced dynamic electron polarisation (DEP) of stable free radicals has been known to be created in both quenching processes of the singlet excited and the triplet excited states by the radicals. The DEP gives enhanced time-resolved EPR signals on the radicals either in absorption or emission phases. The process has been well interpreted by the spin dynamics of the radical-triplet system during the encounter process.^[1] The magnitude of DEP, P_n at each quenching event depends largely on the chemical systems and we found the quenching of triplet xanthene dyes results in significantly large DEP in emission phase by means of time-resolved EPR and pulsed EPR methods combined with the pulsed laser.^[2] This DEP has been utilized in the development of photo-induced NMR signal enhancement procedure.^[3]

The P_n values in radical-triplet systems depend on various factors such as ZFS interaction, diffusion process, exchange interaction of the system and so on. Here we report effects of solvent on DEP in the triplet xanthene dye-nitroxide systems. The P_n values of the systems show clear dependence on the solvent size as shown in Fig. 1a). This dependence is related to the solvent size effect on the triplet quenching rate constant, k_q as given in Fig. 1b). We argue the details of the solvent size effects on unusually large DEP of the triplet xanthene dye systems based on the pulsed EPR analysis of the nitroxide radical signals.

This work is in part supported by the Research Grants Nos. 21K14592, 22K05029, and 21KK0093 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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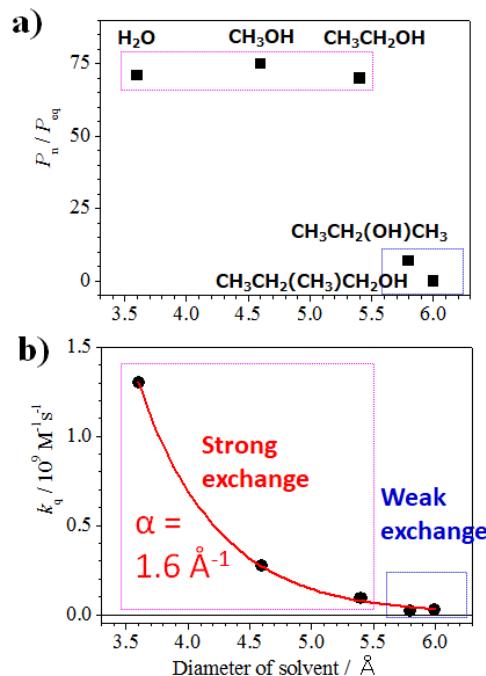


Figure 1. Results of Eosin Y-TEMPO system in various solvents. a) DEP of TEMPO (P_n value) and b) triplet quenching rate constant (k_q value), both are plotted against diameter of solvent.

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Single-molecule readout of spin quantum beats in charge-separated pair states

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To probe the quantum nature of reactions involving radical pairs (RPs) it is helpful to examine the inherent spin quantum beats. However, such beating between singlet and triplet manifolds cannot be measured directly by fluorescence since it takes place in a charge-separated state (CSS), which does not emit light.

Mims et al. recently developed an optical readout technique involving a push laser pulse, which excites the CSS and transfers it into the S1 or T1 state, respectively, following the creating of the CSS by a pump pulse. The CSS is then subsequently converted to either a singlet state, which gives rise to delayed fluorescence, or to a non-emissive triplet state. These measurements were originally performed on a molecular dyad in solution [1].

We have now been able to demonstrate that this measurement is feasible on the single-molecule level by measuring the push-pulse induced delayed fluorescence by time-correlated single-photon counting (TCSPC). We show that the spin state of the single-molecule CSS can be influenced by an external magnetic field, offering the first demonstration of magnetoPL on the single-molecule level.

This work is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (Project ID No. 314695032 – SFB 1277, subproject B03).

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A Comparative Study on Key Factors Influencing Exciplex Emission: Conformation and HOMO of Electron Donor

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Exciplex emission has garnered significant attention for its applications in opto-electric devices and molecular distance sensors.^[1] The electron spin selectivity in exciplex emission between various electron donor-acceptor systems underpins its magnetic field effect through the radical pair mechanism.^[2-3] However, the selection criteria for suitable electron donors and acceptors remain a challenging aspect. In this study, we investigate the critical factors determining the optical properties of exciplex emission for a specific donor-acceptor pair. Utilizing anthracene as the electron acceptor and DMA along with its 6 derivatives as electron donors, we explored the impact of donor's amine group rotation and methyl group substitution in the non-polar solvent, cyclohexane. Our analysis, supported by time-resolved spectroscopy and density functional theory (DFT) alongside time-dependent DFT (TDDFT) calculations, provides an in-depth understanding of these interactions. Contrary to predictions from Rehm-Weller plots, our findings reveal alternative explanations based on the HOMO distribution of the donor, as elucidated by DFT calculations. These results suggest that beyond the redox potential of the acceptor and donor, microscopic structural details and HOMO distribution significantly influence the photoinduced electron transfer (PET) rate and the intensity of exciplex emission. (Figure 1)

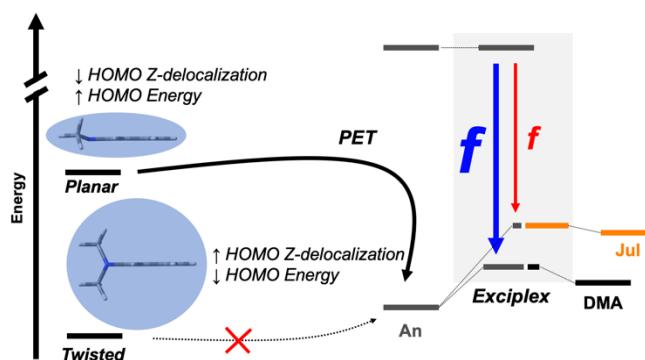


Figure 1. (Left) Relationship between donor molecular conformation (C-N rotation), HOMO energy, and extent of Z-axis delocalization. (Right) Relationship between donor HOMO energy and resulting exciplex HOMO energy. Oscillator strength (*f*) of the exciplex is affected by the contribution of the acceptor (anthracene) to the exciplex HOMO.

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Coherent spin dynamics of radical pairs probed by Pulse and RF magnetic field effect.

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Observing the coherent dynamics of the S-T conversion of electron spins in radical pairs (RPs) is rather difficult because the singlet and triplet spin manifold is not directly accessible by the normal spectroscopic method. The singlet-triplet spin mixing process in radical pairs only becomes apparent when two spins of a radical pair meet and spin selectively react into the different species. Therefore, the spin dynamics of radical pairs is a time-domain convolution of their recombination reaction kinetics, and it has been difficult to see its aspect from time-resolved spectroscopy or to discuss the contribution of decoherence to it, except in some exceptional systems, irradiation chemistry and photoionisation[1, 2]. Recently, Lambert et al. have proposed a new technique called pump-push spectroscopy for the time-resolved detection of the S-T mixing process and have shown the clear time evolution of the S-T mixing process in the rather low field region and clearly interpreted by the theoretical calculations in the specially designed systems[3]. However, the access to the spin mixing process on the commonly produced radical pair system is still very difficult and the electron spin dynamics is only predicted by the theoretical calculation using the expected spin Hamiltonians.

Decoherence phenomena of the spin dynamics of RPs have been discussed rather in the high field regime, due to the spectral shape of MARY[4, 5] and RYDMR[6], and experimental approaches in the very low field regime are very rare. We have recently found that a magnetic field switching method in the low-field regime provides access to the effects of the coherent dynamics of the electron spins, which are thought to be responsible for the low-field effects. However, this feature in the coherent spin dynamics moves to a steady state due to decoherence. This should provide an experimental approach to future discussions on the relationship between magnetoreception and coherent spin dynamics at low magnetic fields.

On the other hand, the spin dynamics in radical pairs can be variably controlled using arbitrary waveform generators (AWGs). Many electron spin manipulations have been performed using AWGs, mainly in EPR. We have performed calculations on chemical reaction control, isotope enrichment, nuclear spin polarisation generation and the possibility of anisotropic chemical reaction control, aiming at chemical reaction control based on spin manipulation by AWGs[7, 8]. Now, we have constructed a TA-detected AWG-RYDMR setup at low and high magnetic fields and have tested the reaction.

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Effect of Molecular Chirality on Radical Pair Spin Dynamics

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The role of chirality in determining the spin dynamics of photoinduced electron transfer in donor-acceptor molecules leading to radical pairs that can function as spin qubit pairs remains an open question. While chirality-induced spin selectivity (CISS) has been demonstrated in molecules bound to substrates, there is no experimental information about whether this process influences spin dynamics in the molecules themselves. Here we use time-resolved electron paramagnetic resonance spectroscopy to show that CISS strongly influences the spin dynamics in two series of isolated covalent donor-chiral bridge-acceptor (D-B χ -A) molecules in which selective photoexcitation of D or A is followed by rapid, sequential electron (Series A)^[1] or hole transfer (Series B) events to yield D $^+$ -B χ -A $^-$. Further, we show that TREPR spectra of D $^+$ -B χ -A $^-$ yield information about the degree to which CISS contributes to the overall spin dynamics that can be ascertained by partially orienting the sample in a nematic liquid crystal (Series A) and even in a randomly oriented powder sample in a frozen glassy solvent (Series B) at cryogenic temperatures. Exploiting this phenomenon affords the possibility of using chiral molecular building blocks to control electron spin states in quantum information applications.

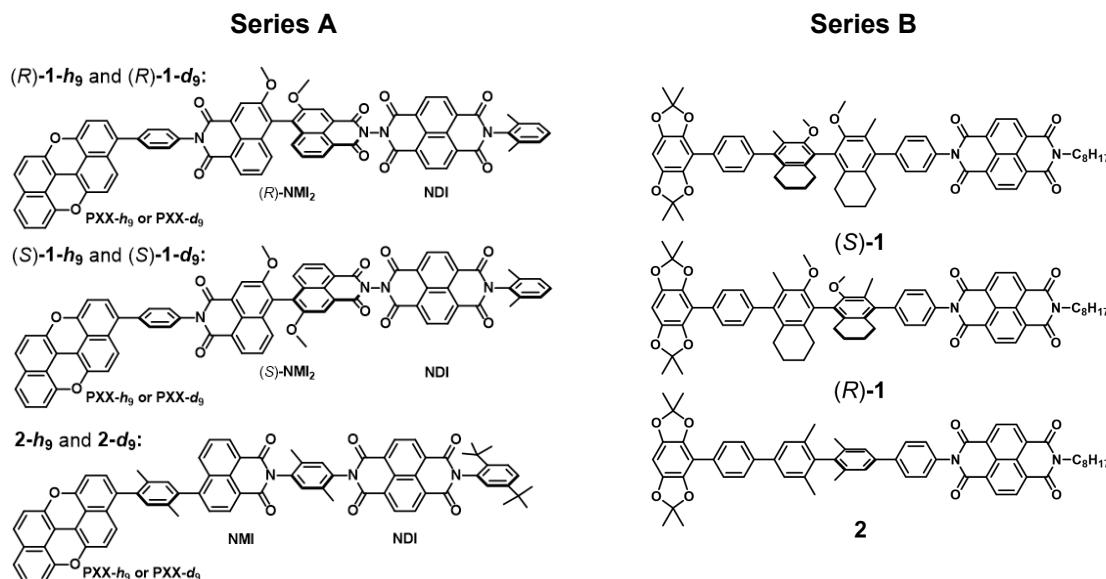


Figure 1. Chiral D-B χ -A and achiral D-B-A molecules in Series A and B.

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Photochemical, EPR and magnetic field effect investigations of a Cry4a avian cryptochrome

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Following their discovery some 30 years ago [1], cryptochromes, a family of blue light photoreceptor proteins, and the radical pairs formed upon their blue light illumination, have taken centre stage in the discussion of animal magnetosensitivity [2].

Here, we explore the radical pairs formed in an avian cryptochrome-4a, using a combination of electron paramagnetic resonance, transient absorption and continuous illumination absorbance and fluorescence spectroscopies. We present a detailed comparison between the wild-type protein and single-point mutants and show that amino acids adjacent to the conserved tryptophan tetrad do not impact the development of magnetic field effects. Conversely, shortening the tetrad by single-point mutation has a dramatic impact on the photochemistry and magnetic sensitivity of the protein [3]. We then discuss possible reasons for this increased magnetic field effect based on the detailed photochemical measurements presented.

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Hyperpolarization Studies of Blue-Light Photoreceptor Proteins

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Paramagnetic intermediates, such as triplet states or spin-correlated radical pairs, are frequently encountered in the blue-light-induced primary responses of photoreceptor proteins containing flavins and derivatives thereof as cofactors. Such species may be favorably probed by their optically generated electron and nuclear hyperpolarizations.

In this contribution we present selected examples of how transient and pulsed electron paramagnetic resonance (EPR) as well as photo-chemically induced dynamic nuclear polarization (photo-CIDNP) NMR contribute to unravelling mechanistic details of the primary processes of flavin and flavin derivatives in (i) aqueous mixtures with redox-active amino acids [1,2], (ii) cryptochrome photoreceptors, a class of flavoproteins involved in the circadian rhythms of plants and animals, as well as possibly in the sensing of magnetic fields in a number of species, and (iii) the light-oxygen-voltage-sensing (LOV) domains, which are protein sensors used to control phototropism, chloroplast relocation and stomatal opening in higher plants [3]. Particular emphasis is on protein variants that have been modified in their amino-acid sequence and/or reconstituted with modified flavins as cofactors.

Acknowledgements: Part of the data presented have been collected by (in alphabetical order) Jing Chen, Nils Pompe, Sabine Richert, Jannis Tesche, and Jakob Wörner, in close collaboration with Prof. Adelbert Bacher (TU Munich), Dr. B. Illarionov and Prof. Markus Fischer and (U Hamburg).

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Optimisation of excitation selectivity in pulse EPR experiments on spin-correlated radical pairs with shaped pulses

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Spin-correlated radical pairs play a significant role in a variety of processes, from natural photosynthesis to photovoltaic energy conversion in organic solar cells, and are being considered for potential applications in quantum sensing. Pulse EPR experiments aimed at characterising spin-correlated radical pairs or exploiting their properties for quantum sensing require precise spin manipulations, and the advent of shaped pulses in EPR spectroscopy has opened up opportunities for improved control of excitation bandwidth and selectivity.^[1]

We have explored the use of narrowband amplitude-modulated pulses for highly selective excitation of a small fraction of spins and the use of broadband amplitude- and phase-modulated chirp pulses for complete non-selective excitation of the full spin-correlated radical pair spectrum on two model donor-bridge-acceptor triads (Fig. 1).^[2] The improved non-selective excitation achievable with chirp pulses compared to standard rectangular pulses leads to increased sensitivity in chirp out-of-phase ESEEM experiments, in particular at higher microwave frequencies. Additionally, broadband excitation combined with echo transient detection allows 2D Fourier-transform-correlated out-of-phase ESEEM experiments containing information not only on dipolar and exchange coupling constants, but also on the relative orientation of donor and acceptor.

In this talk, I will highlight the advantages of shaped pulses in EPR experiments on spin-correlated radical pairs as well as important considerations for their effective use, given the different nature of excitation for chirp pulses compared to monochromatic rectangular pulses.

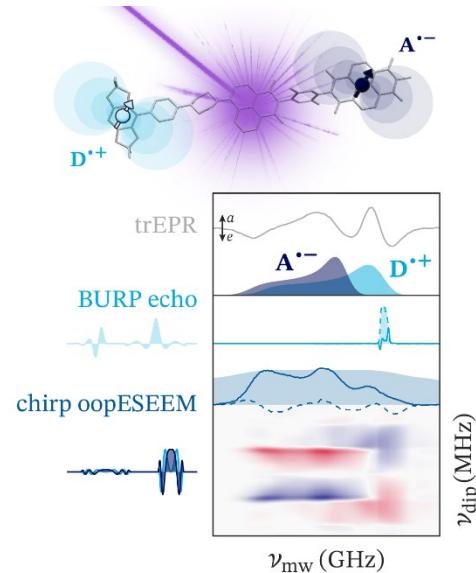


Figure 1. Q-band transient EPR spectrum of the donor-bridge-acceptor triad $\text{BDX}^{\bullet+}$ -ANI-NDI $^{\bullet-}$, simulated spectra of $\text{BDX}^{\bullet+}$ and NDI $^{\bullet-}$, echo Fourier transforms demonstrating narrowband selective excitation with BURP pulses and broadband excitation with chirp pulses and the result of a 2D EPR-correlated chirp out-of-phase ESEEM experiment.

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Study of the Electron Spin of the Triplet Excited States of BODIPY Compounds with Time-Resolved Electron Paramagnetic Resonance Spectroscopy

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The photophysics of organic compounds are usually studied with steady state and time-resolved optical spectroscopic methods, for instance, the absorption and emission spectra. With these spectroscopic methods, the energy gap of different electronic states and the transition probability are characterized. However, electron spin changes upon photoexcitation of the organic molecules, especially in the process of intersystem crossing (ISC) and charge separation, are not characterized by the optical spectra. Moreover, due to the zero field splitting (ZFS) effect, the degeneracy of the three sublevels (T_x , T_y and T_z) of the triplet state (T_1) is lifted, and the population of the three sublevels is usually severely deviated from the Boltzmann distribution, this so-called electron spin polarization (ESP) is informative to reveal the ISC mechanisms. The time-resolved electron paramagnetic resonance (TREPR) spectroscopy can be used to characterize this ESP and to determine the population rates of the three sublevels of the T_1 state.^[1,2] This ESP pattern is very often related to the ISC mechanism, such as the spin-orbit coupling (SOC), or radical pair ISC (RP ISC), etc. Moreover, the spatial confinement of the T_1 state is critical for organic materials used in photovoltaics or electronics. The T_1 state wave function confinement can be also characterized by using TREPR spectra. Recently we studied the ESP and T_1 state wave function confinements of some novel BODIPY compounds,^[3–7] and some insight into the photophysical property of the compounds were obtained with TREPR spectra.

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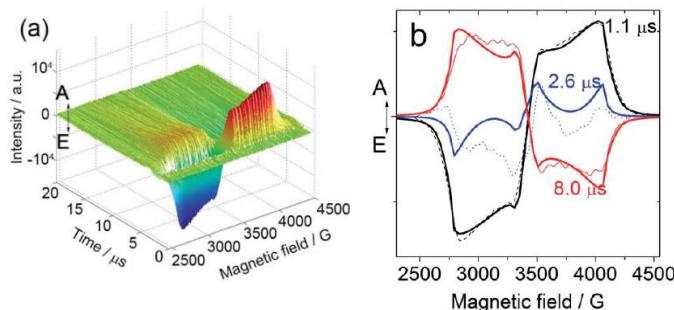


Figure 1. Time-resolved EPR spectra of Styryl-IodoBDP. (a) Full surface of the TREPR spectrum of Styryl-IodoBDP in toluene/2-MeTHF (3 : 1, v/v) at 80 K (excited at 630 nm with a nanosecond pulsed laser) and (b) slices of the surface along the field taken at different delays after the laser pulse td of 1.1, 2.6 and 8.0 μ s.

Verdazyl and triazinyl radicals as multifunctional agents: from spin qubits to selective NO capture

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Stable organic radicals find numerous applications in chemistry and materials sciences, and they have been widely studied and employed for various purposes using EPR spectroscopy. Although a lot of studies concern nitroxide radicals, an increasing attention has been drawn recently to the other types, e.g. trityl, verdazyl and triazinyl radicals.

In a recent series of works we have studied Blatter (triazinyl) radicals grafted onto mesoporous silica material (SBA-15) with the focus on two different applications. In the first one triazinyl radicals act as spin qubits operating at room temperature.^[1] Most qubit candidates known to date are not applicable at ambient conditions, because their phase memory times (T_m) are too short. However, extremely stable Blatter-type radicals localized in the nuclear-spin free porous silica demonstrate record $T_m \sim 2.3 \mu\text{s}$ even at room temperature, thus allowing efficient spin manipulation by microwave pulses. In addition, the mesoporous structure of such composites provides further opportunities for embedding guest molecules into the channels and adding new functionalities. Another application of triazinyl radicals in mesoporous materials aims at selective capture of NO from air, which is a significant ecological challenge. Using EPR spectroscopy we have demonstrated the efficient reversible reaction of Blatter-type radicals with NO, which act as selective NO traps at practical conditions.^[2] Finally, stable mono- and polyyradicals are important building blocks in spintronics. In a recent series of works a number of di-, tri- and tetraradicals based on verdazyl-nitroxide units have been synthesized and studied using EPR, demonstrating their high-spin states and obtaining key spectroscopic parameters.^[3,4] Overall, electron spins of nitroxyl, verdazyl and triazinyl radicals in new combinations, settings, environments open promising directions of further research and applications.

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ns¹ paramagnetic species at the surface

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Controlling matter at the nanoscale allows the development of novel technologies, ranging from quantum information to quantum sensing, optics, cryptography and quantum computing.

At the core of this quantum paradigm is the qubit, a quantum object that can be placed not only on the 0 and 1 states typical of a classical bit, but in any coherent superposition state of the two. There are several physical realizations of qubits that are under investigations, with superconducting circuits technology being at the moment the most advanced.

The spin of paramagnetic molecules and of defects in materials has some appealing properties since it is intrinsically a two-level quantum system, it can be easily manipulated by electromagnetic radiation and benefits of the capabilities of chemists to tune their magnetic and electronic properties through chemical synthesis [1]. Careful choice of the spin-bearing centre, its oxidation state and its surrounding afford a high degree of tunability and permit the modulation of the Hamiltonian parameters, in particular the spin manifold, the magnetic anisotropy and the hyperfine coupling [2,3]. All of these impact the relaxation properties of the qubit. Indeed, a requirement for any system to be a viable qubit is a long coherence time, i.e. a long lifetime of the quantum superposition state. This is an intrinsic property of the system which becomes limiting for practical qubit implementations [1]. All of this can be measured and analysed through Electron Paramagnetic resonance (EPR) spectroscopy methods [4].

Given that to serve as building blocks for a device, spin qubits must be organized on surfaces and preserve long electron spin relaxation times up to room temperature, in this contribution I will focus on exotic S=1/2 spin centres directly bound to the surface of inorganic oxides [5].

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IL18-08

JHPC quantum project for Quantum-HPC hybrid computing platform

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As the number of qubits in advanced quantum computers is getting larger over 100 qubits, demands for the integration of quantum computers and High Performance Computing (HPC) are gradually growing. RIKEN R-CCS has been working several projects to build a platform which integrates quantum computers and HPC together. Recently, we have started JHPC quantum project to design and build a quantum-supercomputer hybrid computing platform which integrates different kinds of quantum computers, superconducting quantum computer from IBM and trapped-ion quantum computer from Quantinuum, with supercomputers including Fugaku. In this presentation, the overview and plan of the JHPC quantum project with a perspective of quantum HPC hybrid computing will be presented.

Generation and transfer of long-lived electron spin polarization between a chromophore and a nitroxide moiety in molecular rulers

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We report a new hyperpolarization mechanism in weakly-coupled radical-triplet spin systems where the chromophore and the nitroxide radical are held at fixed distances.^[1] In this regime, the hyperpolarization of the stable paramagnetic centre can have a major impact in the enhancement of the sensitivity of EPR and NMR techniques, *in primis* light-induced Pulsed Dipolar Spectroscopy.^[2]

A perturbation theory treatment suggests that the interplay between the dynamic Jahn-Teller transitions and the dipolar coupling are responsible for the transfer of electron spin polarization from the photoexcited triplet to the radical probe. Alternatively, large zero-field splitting interactions are the source of net polarization.

Several model systems based on a peptide-template have been considered, where the nitroxide position is progressively changed along the alpha helix (see Fig.1). The chromophores employed are either a Zn-tetraphenylporphyrin, the corresponding metal free base, 2,6-diido-1,3,5,7-tetramethylbodipy or erythrosin B tethered at the extremity of the amino acid sequence.

Importantly, in the Zn-tetraphenylporphyrin-radical conjugates transfer of long-lived electron spin polarization has been achieved, which is an important requisite for polarizing agents.

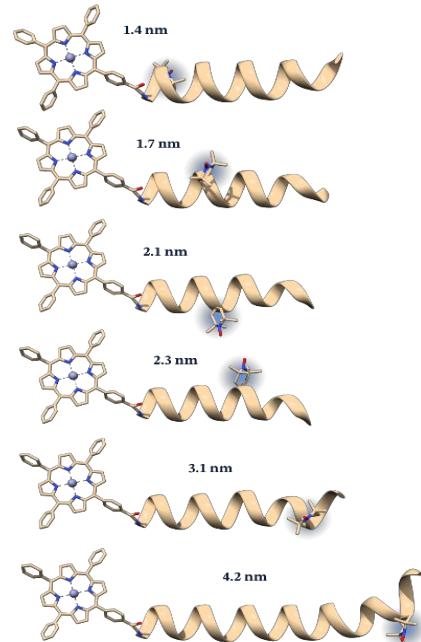


Figure 1. Peptide-based molecular ruler: the increasing distance between the porphyrin chromophore and the hyperpolarized nitroxide moiety is depicted.

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Spin Dynamics of Molecular Spin Qubits by Arbitrary Waveform Microwave Pulses Based on AWG-ESR Technique

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Precise manipulation of quantum states has attracted attention as a key issue in emerging quantum science and quantum information technology. The precise manipulation and the quantum control of qubits are relevant to not only the implementation of fault-tolerant quantum computing and long-term scalable quantum computers but also advance in spectroscopic techniques of magnetic resonance. Molecular spin systems have frequently provided testing grounds for manipulating the quantum spin states by pulsed ESR/ENDOR techniques.^[1] The electron and nuclear spins are controlled by microwave (MW) or RF irradiation pulses. From the technical viewpoint, arbitrary waveform based ESR (AWG-ESR) technology provides advanced methods for flexibly manipulating the spins for particular purposes as well as monitoring the spin behavior under the conditions of the arbitrary pattern of the applied MW or RF irradiation field.

In this presentation, we present application of AWG-ESR technology to stable electron spin qubit systems.^[2,3] We discuss the spin inversion of ESR signals on-resonance for single transition or a spin packet by chirped MW-pulses with swept frequency, focusing on optimization of the passage, i.e., designing pulse schemes enabling it to be as efficient and fast as possible. We demonstrate that almost perfect adiabatic inversion of the spin magnetization can be achieved with relatively short chirped pulses. Such pulses were generated by optimization methods either using the gradient ascent pulse engineering (GRAPE) algorithm with constraints or “constant adiabaticity” sweeps. We also demonstrate that the methods work for an on-resonance spin packet in both homogeneously and inhomogeneously broadened ESR signals, as well as for multi-line ESR spectra.

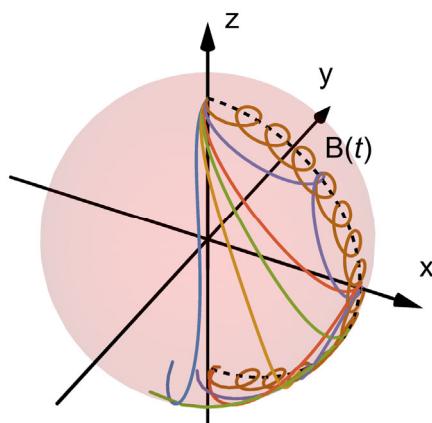


Figure 1. Evolution of the effective field vector, $\mathbf{B}(t)$ (black dashed line), and the spin magnetization vectors, $\mathbf{S}(t)$ (curves in color), induced by chirped pulses in the rotating frame.

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IL19-03

Chemical control of spin coherence in molecular lanthanide complexes

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This presentation will highlight recent work involving optimization of spin coherence and spin dynamics in molecular lanthanide (Ln) complexes. In the first examples, this is achieved through chemical tuning of so-called spin clock-transitions (SCTs)^[1-4] – avoided Zeeman level crossings at which spin dynamics become desensitized to fluctuations (noise) in the local magnetic environment. In this way, SCTs provide optimal operating points at which the electron spin dynamics decouples from the surrounding nuclear bath, leading to enhanced coherence.^[5,6] The SCT frequency can be controlled via crystal-field engineering in the case of integer spin-orbital moments, and the on-site hyperfine interaction in the half-integer case. In the first example, we describe a family of Ho^{III} complexes based on an octadentate cage-like ligand that wraps around the metal center, resulting in a *pseudo*-fourfold molecular geometry, while leaving open an axial coordination site that permits tuning of the SCT frequency, Δ/h .^[1] This approach leads to dramatic increases in Δ relative to prior examples,^[5] thus reducing 2nd-order sensitivity to magnetic noise (which scales as $1/\Delta$). Meanwhile, in the half-integer spin case, we describe several molecular complexes in which the Ln ion adopts the rare 2+ oxidation state such that a lone electron occupies a mixed 5d/6s orbital. Again, ligand design principles enable realization of a doublet ground state with tunable 6s character, resulting in the possibility of engineering the hyperfine SCT gap.^[2,3] This latter approach has the advantage that the unpaired spin resides in an orbital with significantly reduced spin-orbit coupling relative to the 4f shell, giving rise to relatively long spin-lattice relaxation times.

Time allowing, a method employing wideband chirped microwave pulses^[7] will be described for achieving coherent population transfer among the $2S + 1 = 8$ states associated with an $S = 7/2$ Gd^{III} molecular qudit, a key step towards implementing quantum gates using such molecules.

Work supported by the US Department of Energy, Basic Energy Sciences (DE-SC0019330 & DE-AC02-05CH11231), the Office of Naval Research – Global (N62909-23-1-2079), and the US National Science Foundation (DMR-2128556 & CHE-2300779). We acknowledge collaboration with: J. Hrubý, R. Stewart, M. V. H. Subramanya, J. Marbey and K. Kundu (NHFML & FSU); P. Smith and S. Minasian (LBNL); D. Ngo, T. D. Harris and J. R. Long (UC Berkeley); W. J. Evans (UC Irvine); M. Gakiya and M. Shatruk (FSU).

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Spin Manipulation in Magnetic Molecules

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Quantum information technology can realize a new information processing based on quantum mechanics principles. The main systems currently used for quantum computing research include superconducting circuits, semiconductor quantum dots, diamond color centers, and topological insulators. Chemical design can control the quantum behavior of magnetic molecules and obtain a larger Hilbert space. Therefore, studying the quantum coherence of magnetic molecules, performing novel and complex quantum coherence manipulations, and trying to use magnetic molecules for quantum computing are important contents of quantum information materials chemistry. This report will firstly introduce the relevant basic concepts and research ideas of the "Magnetic Molecular Coherence Manipulation", and introduce the "cage structure protection" proposal to enhance the magnetic molecular coherence. The report will also introduce our experiments on efficient coherent manipulation of magnetic molecules using transient electric fields and lasers. The quantum phase interference phenomenon of multi-level molecules of fullerene molecules shows that magnetic molecules have richer physical connotations than traditional quantum systems.

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Structural Insight into Nitric Oxide Reductase Activity of the Diiron YtfE Protein

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This talk presents a detailed study of the YtfE protein in *Escherichia coli*, focusing on its role in converting nitric oxide (NO) to nitrous oxide (N₂O), crucial for protecting iron-sulfur clusters under nitrosative stress. The first part of the study explores YtfE's conformational dynamics, revealing that the protein exists in two states. Using DEER spectroscopy and site-directed spin labeling, it was found that under high osmotic stress, YtfE adopts a uniform conformation (C state), and under moderate stress, it alternates between C and a newly identified C' state, which is key to its NO reduction ability. The second part investigates two substrate tunnels in YtfE, identified as Tunnel 1 and Tunnel 2 using CAVER software. The study shows that both tunnels transport NO, but Tunnel 1 plays a more significant role in substrate movement. Experiments involving steric hindrance, hydrophobic effects, and charge alterations at Tunnel 2 highlight the complex relationship between amino acid properties and enzymatic activity. Overall, this research emphasizes the importance of YtfE's structural conformation in enzymatic function, particularly the NTD's role in facilitating NO access to the diiron core and Tunnel 1's critical role in substrate transport. This comprehensive analysis advances our understanding of YtfE and opens avenues for studying similar proteins, enhancing knowledge of protein dynamics in biological systems.

Photoinduced Ground State Electron Spin Polarization of Different Organic Radicals

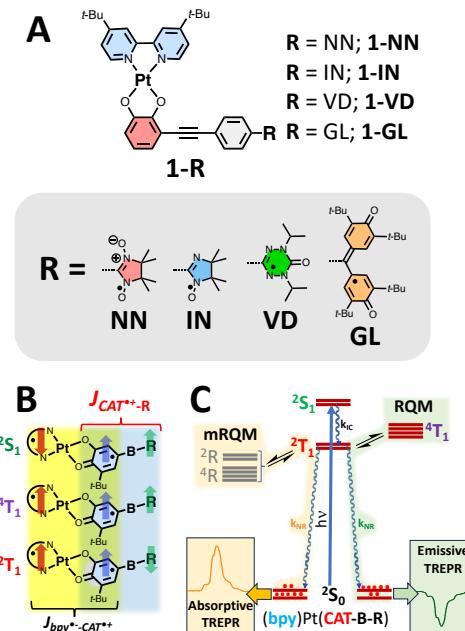
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Stable spin-½ radicals covalently attached to various chromophores are an important class of open-shell molecule for demonstrating a variety of properties and structure-property relationships related to quantum information science. Our efforts have focused on square-planar, d⁸ platinum(II) complexes of catecholate (CAT) donor- and bipyridine (bpy) acceptor ligands in which a nitronyl nitroxide radical is attached to the CAT ligand via an organic bridge fragment (e.g., **1-NN**, Figure A). [1, 2] These complexes exhibit a CAT → bpy, ligand-to-ligand charge transfer (LL'CT) LL'CT electronic absorption band in the visible regions of the spectrum. When a stable radical is attached to the LL'CT chromophore, photoexcitation of the LL'CT band results in a radical-chromophore coupled excited state manifold comprised of ²S₁ (sing-doub), ²T₁ (trip-doub), and ⁴T₁ (quartet) states, Figure B,C. In the absence of a stable radical, these LL'CT complexes undergo rapid charge recombination back to the ground state in under 1 ns. Covalent attachment of a stable radical is also accompanied by fast charge recombination to the ground state, but not before enhanced intersystem crossing from the vertical ²S₁ to ²T₁, followed by equilibration of ²T₁ with ⁴T₁ and/or localized radical excited states (Figure C). Equilibration pathways are enabled by zero-field splitting, energy transfer, or spin-vibronic coupling, and result in non-Boltzmann populations (“spin polarization”) of the ²T₁ m_s-levels. Since the ²T₁ lifetimes are all shorter than the spin-lattice relation times of the stable radical, charge recombination delivers the spin polarization to the ground state where it can be recorded using transient EPR spectroscopy, Figure C. This talk will show evidence of the general utility of our chromophore for polarizing a variety of stable radicals, Figure A.



I₂BODIPY as a new photoswitchable spin label for light-induced pulsed EPR dipolar spectroscopy exploiting magnetophotoselection

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Electron Paramagnetic Resonance (EPR) Pulsed Dipolar Spectroscopy (PDS) using triplet states of organic molecules is a growing area of research due to the unique properties that these transient states afford over stable spin centers, such as increased signal intensity, high orientation selection and switchability. Here we propose the triplet state of a substituted BODIPY moiety (I₂BODIPY) as a spin label in light induced PDS, coupled to a nitroxide, in a model peptide with rigid structure.¹ Orientation selection effects in Laser Induced Magnetic Dipole (LaserIMD) spectroscopy² allow information on the relative orientation of the two labels to be obtained,³ Figure 1. Additionally, magnetophotoselection effects in I₂BODIPY enable optical orientation selection of the chromophore triplet state generation, yielding additional constraints for the determination of the relative orientation of the spin labels.¹

This work was supported by the Royal Society (DH160004, DHF/R/221018, /R1/180099, RGF/EA/201050, RGF/EA/201050 and RF/ERE/210351), the Royal Society of Chemistry (CAMS Fellowship 2020 ACTF ref. 600310/09), the EPSRC (EP/L011972/1, NS/A000055/1, EP/W014521/1, EP/V035231/1, and EP/S033181/1), the University of Padova (P-DiSC#04BIRD2019-UNIPD), Centro Studi “Giorgio Levi Cases” (Biomolecular DSSCs) and the Italian Ministry for University and Research (PRIN 2022NMSFHN).

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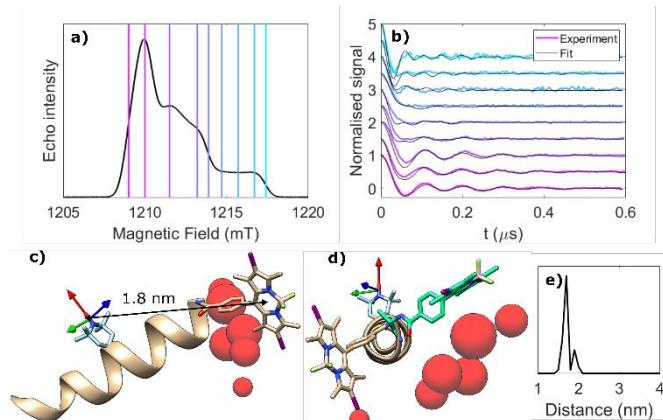


Figure 1. (a) Electron spin-echo field-swept spectrum showing the magnetic field values where LaserIMD traces were acquired. (b) Background-corrected and modulation depth-normalised LaserIMD traces (coloured lines) and orientation-dependent model-based fits (black lines). (c) DFT-optimised structure of model peptide showing the positions of the I₂BODIPY centre as red spheres, relative to the nitroxide g-tensor frame. (d) Projection view of panel (c), including a second local energy minimum conformation (+ 9 kJ/mol, green). (e) Distance distribution between the centres of the spin-bearing moieties.

Exploring Unusual Molecular Architectures with EPR Spectroscopy

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Abstract: This presentation will feature mostly unpublished results from steady-state and time resolved (CW) electron paramagnetic resonance spectroscopy experiments on stable and transient radicals in unusual environments. The talk will emphasize the breadth of different structures that can be investigated, which include microbubbles, nanocrystals, and vesicles, to learn about structural and physical properties of these systems. Significant attention will be paid to new results on spin probes studies of structured (non-Newtonian) fluids constructed from AerosilTM nanoparticles in organic solvents, seeking to understand the influence of solvent-solvent, solvent-Aerosil, and Aerosil-Aerosil interactions as a function of Aerosil loading, solvent, and temperature. Spin probe measurements in microbubbles reveal orientation effects in the outer layer of these structures for the first time. In nanocrystals we show strong evidence for the presence of radical pair triplet states. The vesicle experiments suggest new directions for small molecule topology in supramolecular systems. In structured fluids, there are significant effects on spin probe rotational behavior as a function of Aerosil loading, solvent, and temperature that will be presented and discussed.

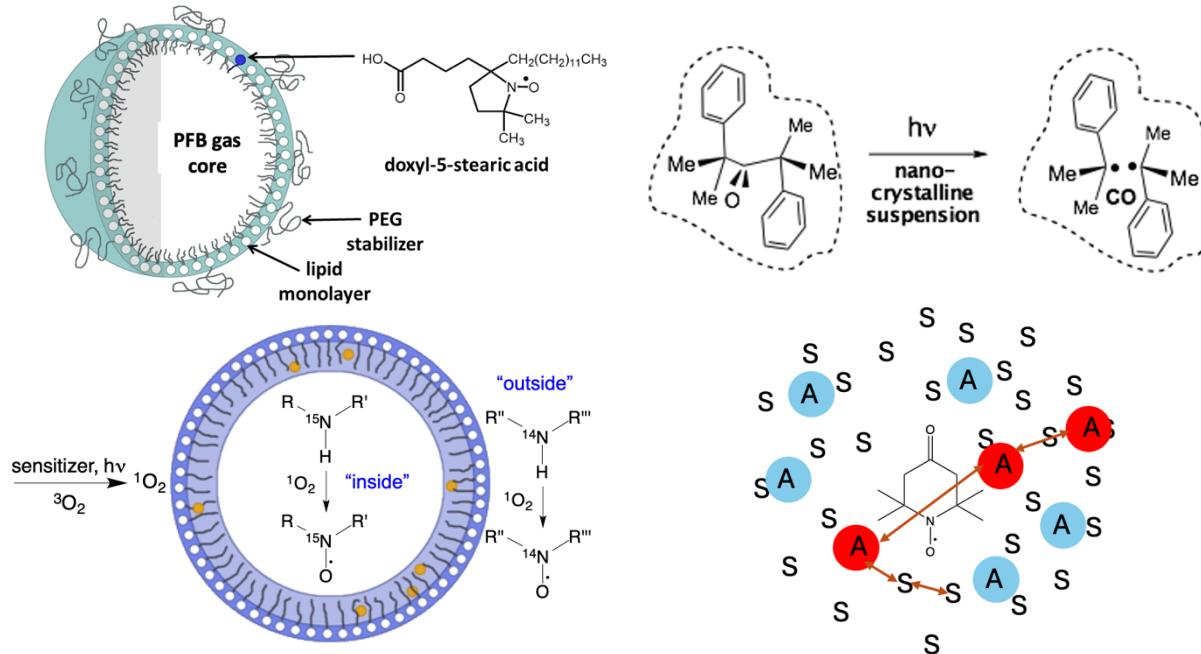


Figure 1. Top left: spin probes in microbubbles. Top right: transient radical pairs in nanocrystals. Bottom left: spin probes in vesicles. Bottom right: spin probes in Aerosil-based structured fluids.

Funded by the U.S. National Science Foundation (Grant # CHE-1900541).

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Electron Spin Polarization Induced by Triplet-Triplet Annihilation in a Photon Up-conversion System

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The photon up-conversion (UC) technique, based on triplet-triplet annihilation (TTA), has garnered significant interest in various research fields related to light-to-energy conversion technologies. This method allows the creation of emissive singlet exciton from two triplet excitons generated by irradiating low-energy incoherent light. However, the precise mechanism by which two triplet excitons are converted into an emissive singlet exciton remains incompletely understood. To gain insight into the spin conversion process, it is essential to investigate the spin state of the triplet exciton during TTA. Electron spin polarization (ESP) observation provides valuable information about the local electronic structure of the exciton. In this study, we conducted time-resolved electron paramagnetic resonance (TREPR) measurements on an efficient liquid TTA-UC system comprising platinum-octaethylporphyrin (PtOEP) as the photosensitizer and 9,10-diphenylanthracene (DPA) as the TTA emitter. Our goal was to reveal the spin dynamics of the TTA-UC process. Figure 1a shows the TREPR spectrum of the DPA/PtOEP system in toluene at room temperature following light excitation (532 nm) using a pulsed laser. The absorptive EPR signal originates from the triplet exciton of DPA. The spectral linewidth narrows due to the motional narrowing effect in the low-viscosity medium. Figure 1b shows the time profile of the EPR signals at 340 mT. The time evolution depends on the triplet concentration of DPA, rate constants of chemical reactions, and spin-lattice and spin-spin relaxation times. Our analysis, employing modified Bloch equations that describe chemically induced ESP, revealed that TTA induces significant ESP in the DPA triplet. This finding suggests efficient spin interconversion within the triplet pair state.

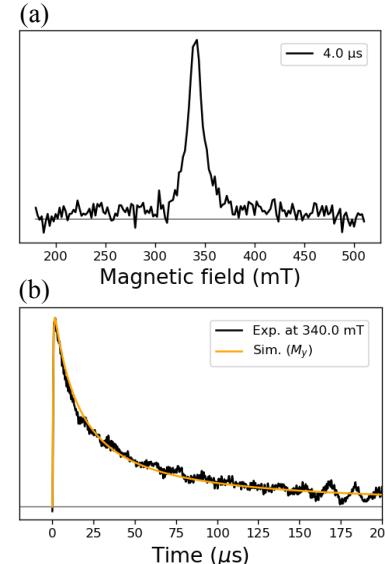


Figure 1a) TREPR spectrum of DPA/PtOEP in toluene at room temperature. b) Time-profile of the EPR signal obtained at 340 mT (black) along with the simulation (orange) calculated by solving the modified Bloch equations.

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Triplet Fusion of Diphenylanthracene in Fluid Solution and Crystalline Solid

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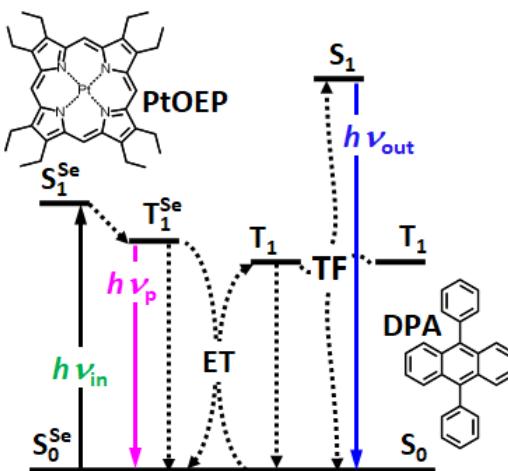
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Triplet fusion (TF) has recently attracted a great deal of attention from the various application viewpoints, such as organic solar cell, organic light-emitting diodes, photochemistry, bioimaging and others, because TF following triplet energy transfer (ET) from a sensitizer (Se) achieves photon-upconversion (PUC). As illustrated in Scheme 1 of PUC, incident low-energy photons ($h\nu_{in}$) absorbed by Se are converted to high-energy photons ($h\nu_{out}$) generated by TF. The TF merges the electronic energies of two molecules in the excited triplet (T_1) state into one molecule in the excited singlet (S_1) state by electron exchange. Since the TF occurs via the contact pairs (TT) formed by encounter of two molecules in the T_1 state, the triplet exciton dynamics play an essential role in the PUC. Actually the importance of triplet dynamics is pointed out in many studies on TF in both liquids^[1-4] and solids.^[5-8] However there are no comprehensive study on the TF in the liquid and solid phases. Therefore, in this paper, we measured the TF-derived fluorescence of 9,10-diphenylanthracene (DPA) that initiated by the ET from the T_1^{Se} state of platinum octaethylporphyrin (PtOEP) in a fluid solvent of tetraethylene glycol dimethyl ether and in DPA polycrystal, in order to clarify the effect of triplet exciton diffusion on the TF. It has been elucidated that not only translational diffusion, but also rotational diffusion seriously affects on the TF efficiency in fluid solution phase. In solid phase, we observed the triplet exciton diffusion explained by the multiple trap model^[8] and a temperature-dependent magnetoluminescence effect suggesting a charge-transfer interaction for the TF of the TT pair.



Scheme 1 Energy diagram of DPA and PtOEP and PUC dynamics involving ET followed by TF.

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A Time-Resolved EPR Study of the Lowest Excited States of Copper(I) Heteroleptic Complexes by Using X- and Q-band Frequencies

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Heteroleptic copper(I) complexes which exhibit intense visible emission attract considerable attention due to their potential application to OLED, sensors and photosensitizers for photo-energy conversion processes. While homoleptic phenanthroline copper(I) compounds are a little unstable in the excited state, heteroleptic copper(I) complexes bearing phenanthroline and diphosphine ligands are expected to be utilized due to their longer lifetimes of the lowest metal-to-ligand charge transfer (MLCT) excited state. Various attempts have been made to prolong lifetimes further and to stabilize the CT excited state. Since luminescence from the copper (I) complexes at ambient temperature is a superposition of phosphorescence and delayed fluorescence, it is crucial to know the structure and dynamics of the lowest excited triplet state.

Time-resolved(TR) EPR is promising tool to examine the excited multiplet states. Generally, CT excited states involving a transition metal ion show large zero-field splittings (ZFS), it is difficult to observe their TREPR spectra. However, in the case of the copper (I) complexes, we have succeeded to detect TREPR signals for several complexes. Features of TREPR spectra of the Cu(I) complexes observed at 15 K in butyronitrile or 2-methyl tetrahydrofuran solutions upon the laser excitation at 415 nm are very unique and different from typical triplet spetcra, depending upon the ligands. TREPR measurements on X- and Q- band frequecncues enabled us to simulate the obverved TREPR spectra, because ZFS parameters affect X and Q and spectra in the same way while g-values cause effects differently. Complexes having a large ZFS parametres ($|D| \sim 1 \text{ cm}^{-1}$) give almost no structure of X band spectra but give structures in Q band. In contrast, TREPR spactra for complexes having smaller ZFS ($|D| \sim 0.2 \text{ cm}^{-1}$) exhibiting structure in X band. Phenanthtoline as well as diphoshine ligand dependence is discussed in terms of contribution of ligand-to-ligand (LL) CT and (π, π^*) excited state into the lowest metal-to ligand CT state.

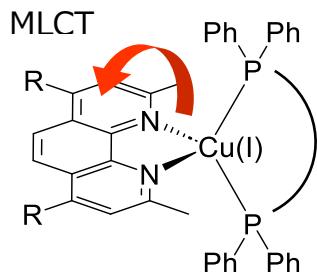


Fig. Structure of heletoreplic Cu(I) complexes bearing phenahthroline and diphosphine ligands

Quantum Sensing of Magnetic Fields with Molecular Spins.

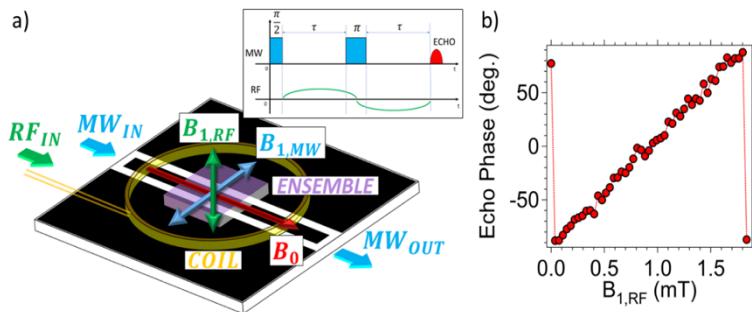
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To prove that molecular electron spins hold potential for quantum technologies, we have recently shown that it is possible to embed molecular spin ensembles into planar superconducting microwave (MW) resonators [1] and to coherently manipulate them though resonators by using suitable sequences of MW pulses [2], eventually down to sub-nanoliter sample volumes [3]. Molecular spins can work also as temporary memories for information [2], in which the readout of output signal/s can be further assisted by machine learning methods to improve either amplitude or phase inference [4]. Due to their long coherence time, the relatively easy possibility of manipulation and readout and their intrinsic quantum nature and properties (such as entanglement), molecular spins have been proposed also for quantum sensing schemes [5]. However, experimental demonstrations of sensing schemes involving such spins have not been reported yet.

Here we test molecular spins for quantum sensing of magnetic fields [6]. To this end, we first consider a diluted VO(TPP) molecular spin ensemble embedded into a planar MW superconducting resonator, as in Fig.1.a. The sensing protocol consists in a MW pulse sequence which is used to coherently drive the spins and to obtain a Hahn's echo, while the radiofrequency (RF) signal to be detected is sent during the free spin precession time through an additional RF coil. We show that it is possible to detect changes in both echo amplitude and phase and to relate them to the presence and the parameters (amplitude, phase) of the RF field, as in Fig. 1.b [6]. We extend our sensing protocol to the case in which Dynamical Decoupling sequences, such as Carr-Purcell-Meiboom-Gill [2] and Period Dynamical Decoupling are used, and we apply them to drive an ensemble of diluted BDPA organic radical [6,3]. The effect of the RF field on the echo is found to increase with the number of π pulses used in the MW sequence. The resulting magnetic field sensitivity can reach values as high as nT/\sqrt{Hz} with a relatively low number (4-5) of π pulses applied, which is comparable with the typical values reported for Nitrogen Vacancy centers magnetometry performed through Optically Detected Magnetic Resonance spectroscopy [6]. These results show, for the first time, quantum sensing protocols can be successfully implemented with molecular electron spins.



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Magnetic field effects on triplet pairs in organic crystals

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Singlet fission and triplet-triplet annihilation have attracted much attention in recent years due to their potential application to organic photo devices [1-4]. In both processes, triplet pairs (TPs) are generated as an important intermediate. Spins in TPs can be modulated by the application of an external magnetic field. Fluorescence after triplet-triplet annihilation shows remarkable magnetic field effects (MFEs) [5-8]. The observation of magnetic field effects on fluorescence in organic crystals was the only method to investigate singlet fission and triplet-triplet annihilation until the 1980s and has remained a powerful tool since the 1990s.

In this contribution, we study MFEs on fluorescence from organic crystals under high magnetic fields up to 10 T. In addition to the known MFEs associated with separated TPs, we observed MFEs caused by the avoided-level crossing (ALC) between spin states in exchange-coupled TPs [6-8]. We determined the magnitudes of exchange interactions in TPs generated by singlet fission and triplet-triplet annihilation in several organic crystals. The detailed analysis of exchange coupled TPs has demonstrated that spin state mixing is promoted by anisotropic dipole-dipole interaction in a triplet exciton. Thus the observed MFEs due to ALC also contain detailed information on orientations of TPs. The structure of triplet pairs can be discussed with the analysis of MFEs caused by ALC.

MFE measurements can also be used to reveal the reaction pathway of TPs in organic solids. As in the case of OLEDs, spin multiplicity is one of the limiting factors to improve the efficiency of up-conversion assisted by triplet-triplet annihilation (TTA) [9]. TTA in organic materials can produce the excited single state from the singlet TP and the excited triplet state from the triple TP. Since the excited triplet state is generally non-luminescent, the generation of the excited triplet state reduces the efficiency of up-conversion. However, the direct observation of the excited triplet state produced by TTA has been difficult because the reactants and products are the same, and the generation of the excited singlet states and the excited triplet state are both second order. We measured MFEs on fluorescence in crystalline 9,10-diphenylanthracene, which is frequently used in up-conversion studies. Our high filed MFE study has demonstrated that both excited singlet and triplet states are efficiently produced by TTA in crystalline 9,10-diphenylanthracene.

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The Varied (and Exotic...) Radical Pair and Spin Dynamics of Vitamin B₁₂Alex R. Jones¹¹ National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW110LW, UK

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The active derivatives of vitamin B₁₂ (cobalamin, Fig. 1a) serve as cofactors to metabolic enzymes and light-dependent transcriptional regulators, and are strongly associated with radical chemistry. Because of the central cobalt ion, the radical pair (RP) and spin dynamics have some exotic properties, the nature of which are highly dependent on its environment and axial ligation.

Photolysis of 5'-deoxyadenosyl cobalamin (AdoCbl) and methylcobalamin (MeCbl) gives cob(II)alamin / alkyl RPs.^[1] The large difference in hyperfine couplings result in sub-nanosecond spin-state mixing times and hence MFEs on ultrafast timescales (Fig. 1b).^[2] A similarly large difference in *g*-values means that MFEs owing to the Δg effect occur at unusually low MF exposures (Fig. 1b). Rapid diffusion of the small Me radical results in spin polarized TREPR signals with

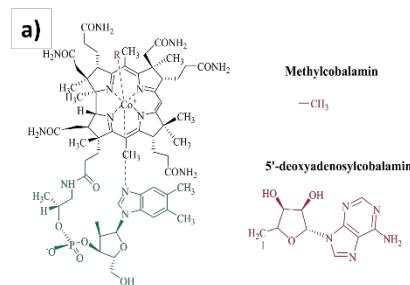
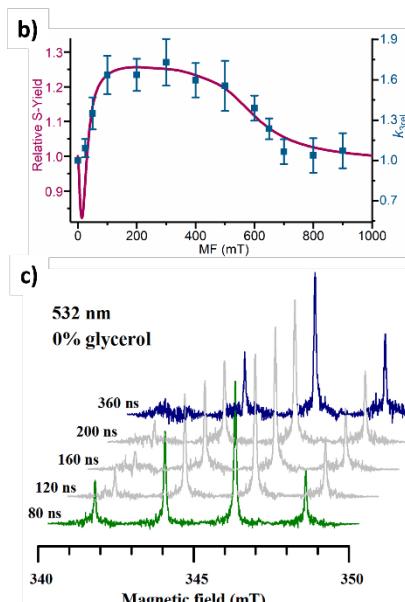


Figure 1. a) Active derivatives of B₁₂ and their axial ligands. b) TREPR spectra following the photolysis of MeCbl. c) MARY curve of the ultrafast radical pair reaction dynamics following the photolysis of AdoCbl.

contributions from both geminate pairs and Me/Me *f*-pairs (Fig. 1c).^[3] When bound to B₁₂-dependent enzymes, the MFE on AdoCbl photolysis increases in magnitude owing to the binding pocket serving as a RP cage.^[4] Magnetic-sensitivity is lost, however, when the same Ado/cob(II)alamin RP is generated thermally upon substrate binding to AdoCbl-dependent enzymes, owing to a forward commitment to catalysis. The light-dependent transcription regulator CarH stabilizes charge transfer states within AdoCbl,^[5] avoiding radical products completely.^[6]



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IL19-15

Time resolved fluorescence microscopy of biological radical pairs

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Understanding of the importance of the role of radical pairs in biological systems is increasing. For example, the radical pair mechanism is believed to explain the ability of migratory birds and other animals to sense the geomagnetic field (e.g. [1]), radical pair based magnetic field effects have been observed on cellular autofluorescence [2] and new genetically modified proteins with large magnetic field responses have been developed which pave the way for a new field of magneto-optogenetics [3].

In order to properly investigate the role of radical pairs in biological systems, techniques are necessary that can allow the direct observation of radical pair kinetics with sub-micron spatial resolution, time resolution of tens of nanoseconds, for radical pairs generated from precursors at endogenous cell concentration levels ($\sim 10\mu\text{M}$). We have developed a single colour, two pulse laser based microscopic technique that achieves these requirements, allowing the direct time dependence of radical pairs to be observed based on precursor fluorescence. This technique when used in combination with a nanosecond rapidly switched magnetic field, provides a suite of techniques to study radical pairs in biological systems.

We present experimental and theoretical demonstrations of the utility of this technique and its application to both established photochemical radical pair reactions and in systems of direct biological significance.

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A1-01

Boost of the reaction yields with AWG-RYDMR at low magnetic fields

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The control of radical pair reaction is an important subject applied to the improvement of luminescence efficiency of organic light emitting diodes (OLEDs), isotope enrichment and the elucidation of quantum mechanical mechanisms underlying reactions in living organisms. The method of observing the yield change of reaction products of radical pairs in a magnetic field with the application of an oscillating magnetic field (RF) is called reaction yield detected magnetic resonance (RYDMR), and a single-color RF has been used for RYDMR. However general radical pairs have multiple nuclear spins, it is difficult to induce transitions in all nuclear spin configurations with a single-color RF, and there are also limitations such as spin locking when trying to cover the frequency with RF intensity. To overcome this problem, we have developed a method to control RP by irradiating waveforms based on the local optimization theory^[1] from an arbitrary waveform generator (AWG)^[2,3]. Here we report the experimental AWG-RYDMR results for the BSA-AQDS system in a transient absorption detection RYDMR system with the introduction of AWG.

For the evaluation of RYDMR effects (ΔMFE), the magnetic field effects of transient absorption (ΔA) during RF irradiation (MFE_{on}) and during non-irradiation (MFE_{off}) were defined as follows.

$$MFE_{on/off} (\%) = 100 \times \int \frac{\Delta A(B, B_1^{on/off}, t) - \Delta A(0, B_1^{off}, t)}{\Delta A(0, B_1^{off}, t)} dt$$

$$\Delta MFE (\%) = MFE_{on} - MFE_{off}$$

The arguments of ΔA correspond to the applied static magnetic field B , the oscillating magnetic field B_1 on/off, and time t , respectively. Fig. 1 (a) shows the B_1 spectrum in a resonance field (5.17 mT) of single-color RF (145 MHz). ΔMFE decreases with increasing B_1 , but the signal is inverted around $B_1 = 0.4$ mT. This is due to spin locking and confirms that there is a limit to the yield change in single-color RYDMR. Fig. 1 (b) shows the field swept RYDMR spectra of single-color RF ($B_1 = 0.34$ mT) and periodical chirp RF (145±15 MHz FM frequency 10 MHz). The yield change near resonance field by chirp RF is larger than that by single-color RF. This phenomenon can be explained by the coverage of the hyperfine structure and the effect to the spin locking by the chirp RF. The details of the AWG-RYDMR setup and frequency modulation techniques will be discussed on the day.

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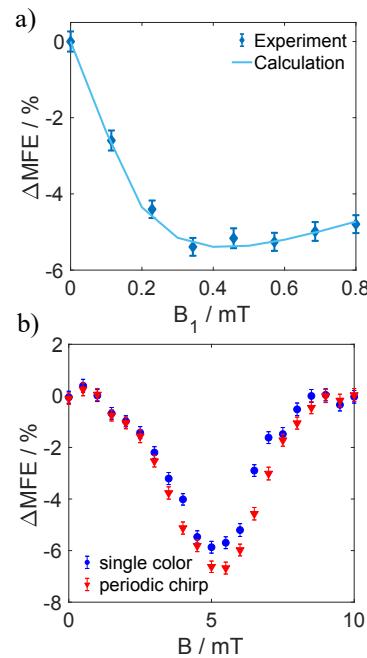


Figure 1. a) B_1 dependence of RYDMR signal in BSA-AQDS system ($B_0 = 5.17$ mT), b) RYDMR spectra with chirp RF and single-color RF.

Modulation of quantum coherence of triplet qubit through guest-responsive structural change of a metal–organic framework

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Quantum sensing is a method to use quantum properties of quantum bits (qubits) to improve the sensitivity and the resolution beyond the classical sensing.^[1] Electron spins of molecules have been extensively studied as qubit (molecular qubit) because of their high tunability and homogeneity of structures. One strategy to make the system responsive to analytes is employing porous materials such as metal–organic frameworks (MOFs). Although quantum sensing of molecular qubit in MOFs are reported, the sensing targets are limited to specific atoms or molecules.^[2] Detecting change of the coherence time (T_2) of qubit is a promising method known as relaxometry to sense various chemicals because the coherence time can be modulated by alternations of the surrounding environments. However, significant relaxation is induced by the motion of qubit itself because it is exposed to MOF pores, and it is necessary to achieve both sufficiently long T_2 and the responsivity.

Here we utilized triplet electron spin of diazatetracene (DAT) as qubit and loaded it in a flexible MIL-53 MOF (Fig. 1a).^[3] Triplet electron has not only a relatively long T_2 but also a large spin polarization suitable for qubit initialization. Some guest molecules are introduced into the pores in addition to DAT qubit and T_2 of DAT was measured by a pulsed EPR. In general, the introduction of guests shorten the T_2 because of the increasement of hyperfine couplings. Nevertheless, when some guest molecules are added, the T_2 of DAT was drastically increased. To investigate the main factor of the spin–spin relaxation process, the guest occupancy around DAT was estimated. It was found that higher guest occupancy leads to longer T_2 (Fig. 1b), indicating that the qubit motion affected the decoherence process of DAT. Molecular dynamics simulation also supported that the motion of DAT was largely limited in the presence of guests.

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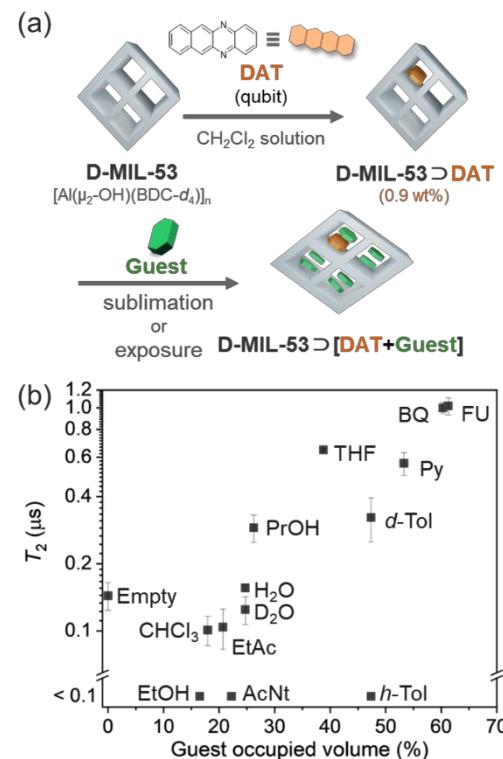


Figure 1. (a) Accommodation of DAT and guests into MIL-53 nanopores.

(b) T_2 against guest occupancy in the pore.

Study of diffusion in metal–organic frameworks by spin-probe approach

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Metal-organic frameworks (MOFs) are perspective materials, which can be applied in many fields of industry such as catalysis, selective sorption, separation and many others. Such application are possible owing to many tunable cavities that act as active centers, and, as a consequence, high porosity of the material. All industrial processes must be time-efficient. Hence, the diffusion rate of molecules to the cavities (active centers) of MOF powders and pellets is a crucial parameter for practical use.

Because of low spatial resolution, most of techniques can't distinguish intra-particle and inter-particle diffusion in MOF powder, the common form of material. It becomes more challenging when we need to study diffusion into the cavities of MOF pelleted composite, which is more convenient form for industrial use. To overcome these limitations, we've employed spin-probe Electron Paramagnetic Resonance (EPR) to study solvent diffusion into both powders and pelleted composites. The method of MOF synthesis allow us to place sensible to the environment and visible for EPR spectroscopy spin-probe into the cavity without changing the structure of material. Spin-probe is trapped into the MOF cavity and can't leave it, allowing us to selectively monitor the impregnation of the cavities during experiment. After mathematical modeling of EPR spectrum taken in different times, kinetic curve and corresponding diffusion coefficients can be obtained for the molecules of interest.

It was reasonable that the diffusion rate into MOF pelleted composite depends on kind of MOF, binder and plasticizer. However, we've established that diffusion properties of the material strongly depends on preparation procedure even in case of same MOF, binder, plasticizer and their amount. We explained the phenomenon to the decreasing on-surface MOF particles blockage by binder. Particle size of MOF takes place in the uptake of guest molecules as well. Nanoparticles usage instead of macroparticles for pellet preparations leads to faster diffusion rate.

Studying ways of shaping procedure optimization upon EPR control yields robust pellets with pore filling rates comparable to those for powdered MOF. The proposed methodology is promising for future application in shaping and diffusion optimization of various MOFs for industrial application.

This work was supported by the Russian Science Foundation (No. 22-73-10239).

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EPR study of interactions between paramagnetic nitric oxide and radical doped porous materials

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Abstract

Developing methods for capturing nitrogen oxides ($\text{NO}_x = \text{NO}$ and NO_2) is a significant environmental challenge. One potential solution involves using stable radicals grafted onto the surface of nano- and mesoporous materials that can interact reversibly with nitrogen monoxide. Electron paramagnetic resonance (EPR) spectroscopy is generally the most suitable technique for studying radical-containing materials. Additionally, EPR is a versatile tool for characterizing the sorption mechanisms of paramagnetic gases, such as NO_x , in porous media.

In this research, we studied the interactions (chemisorption and physisorption) between nitric oxide and radical-doped porous materials using EPR spectroscopy. We examined several materials to better understand the factors influencing the sorption process: Blatter radical-containing silica robust materials, xerogels, SBA-15, and MOF-808. Our results demonstrated for the first time that Blatter radical-containing materials are able to interact with NO, forming a diamagnetic product^[1]. We found that the sorption properties of these paramagnetic materials vary significantly depending on the synthesis conditions and structural features. We studied desorption by heating to different temperatures and monitored the change in radical centers using EPR. Quantitative EPR analysis of radical content during repetitive sorption/desorption cycles revealed sustainability of the sorption capacity for both xerogels and SBA-15. EPR spectroscopy confirmed the selective capture of nitric oxide from a flue gas model mixture by radical-containing xerogel.

This work was funded by RSF (No 22-73-10239).

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Detection of Radical Pairs via Fluorine photo-CIDNP

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Fluorine-containing flavin derivatives can be used as probes in flavin-binding proteins forming radical pairs via photo-chemically induced dynamic nuclear polarization (photo-CIDNP) NMR. Knowledge of the hyperfine structure is crucial for studying the formation of intramolecular radical pairs in proteins, since the signal intensity depends on the hyperfine coupling.^[1] Transient fluorine photo-CIDNP was used to determine the isotropic hyperfine coupling constants of fluorine nuclei in 6-fluoro-7,8-didemethyl-FMN, 7-fluoro-8-demethyl-FMN and 8-fluoro-7-demethyl-FMN (see Fig. 1a and c). Combining this method with transient proton photo-CIDNP spectroscopy leads to a more accurate interpretation of the intermediate radical species that form a radical pair. The gathered information is used to identify the most promising flavin derivative for usage as a probe for detection of radical pairs in proteins.

The LOV2 domain from *Avena sativa* forms a flavin–cysteinyl adduct after blue-light irradiation.^[2] Mutation of the cysteine-450 to an alanine yields a radical pair of the flavin with an adjacent tryptophan upon photoexcitation instead.^[3] Using fluorine CIDNP, detection of a strong signal of the incorporated 8-fluoro-7-demethyl-FMN was possible in only 8 scans, which takes about one minute of measurement time (see Fig. 1c). The observed polarization is a footprint of the intramolecular radical pair. By comparison, 1024 scans were necessary to record the depicted spectrum without illumination, which still has a worse S/N ratio. This approach is very promising in cases where photostability or sensitivity limit the possible amounts of scans.

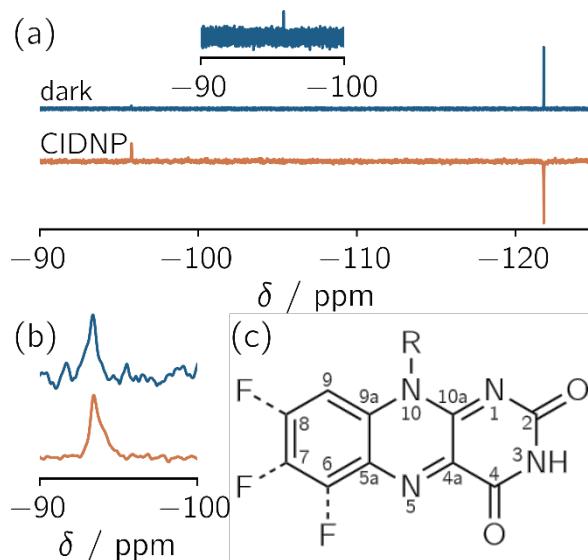


Figure 1: Dark (blue) and CIDNP (orange) spectra of 8-fluoro-7-demethyl-FMN in solution with 6-fluorotryptophan (a) and incorporated into a cysteine-devoid LOV2 domain from *Avena sativa* (b). The insert in (a) shows the dark signal of the fluorinated flavin. The studied flavin derivatives were fluorinated in either 6-, 7- or 8-position of the isoalloxazine moiety (c).

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Optically Generated Hyperpolarisation in Solution-State Magnetic Resonance

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A newly developed approach to solution-state dynamic nuclear polarisation (DNP) uses optical illumination instead of microwave pumping [1]. Upon illumination of a suitable dye, a long-lived triplet state is formed, which can undergo spin-selective quenching with radicals in solution to generate dynamic electron polarisation on the radical via the radical triplet pair mechanism (RTPM) [2]: i) the triplet dye and radical can diffuse together to form a doublet-quartet pair in an encounter complex, ii) this encounter complex lives long enough to generate substantial polarisation of the radical's electronic transitions due to spin-allowed relaxation from the doublet manifold. Subsequent cross-relaxation of the radical with nearby protons produces in-situ nuclear polarisation [1]. Persistent radicals, such as TEMPO, can be used in the RTPM, avoiding any competitive kinetic decay processes that affect other mechanisms of generating chemically induced dynamic electron polarisation (CIDEP).

The work presented applies a method of rapid mechanical shuttling of NMR samples on a benchtop spectrometer from low to high magnetic field strengths [3], to generate sensitivity enhancements in solution state NMR using the RTPM. Illumination of the sample occurs at low-field where the RTPM and subsequent cross-relaxation is most efficient, with sample transfer to higher field for improved chemical shift dispersion (see Fig. 1). Sample transfer occurs on the sub-second timescale, minimising any nuclear relaxation. We present preliminary findings comparing enhancements generated using different chemical systems, and the optimal magnetic field for polarisation in the shuttle system. Finally, we present time-resolved EPR data which gives an insight into pH and salt effects on the RTPM, first explored in DNP studies.

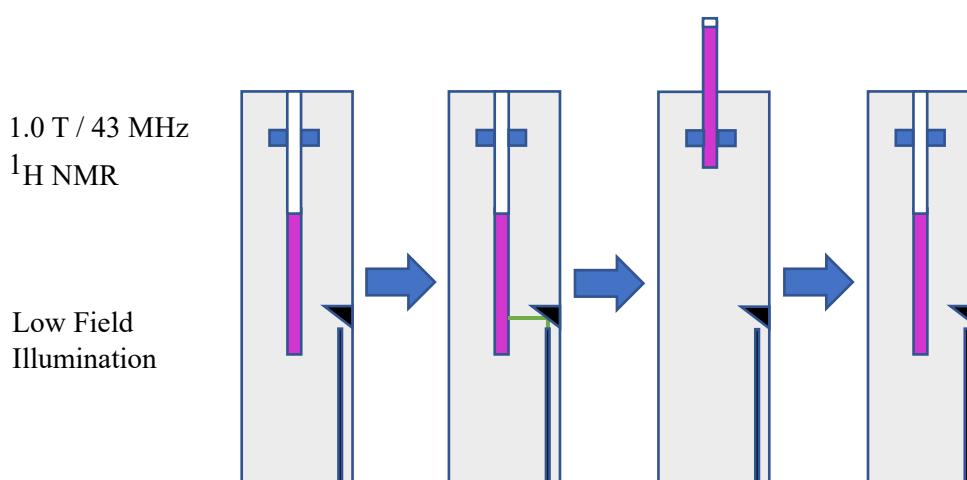


Figure 1: A pictorial representation of the shuttle and illumination system developed.

We gratefully acknowledge financial support for this work from the Royal Society [IEC\R3\213064] and Royal Society of Chemistry [E21-3124554325]

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Temperature dependant electron nuclear double resonance (ENDOR) studies of Hydrogen Atoms in Silsesquioxane Cages

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

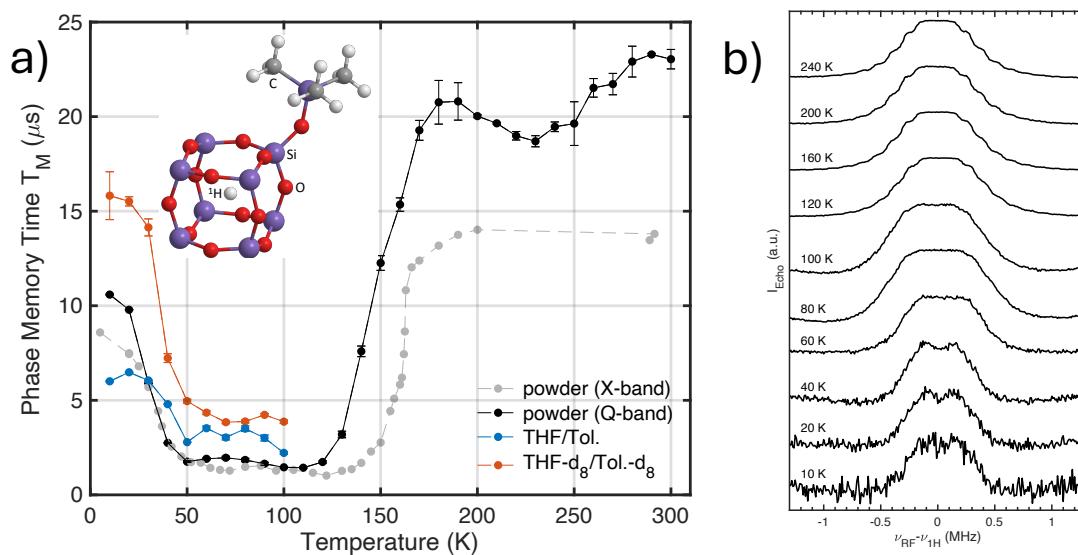


Figure 1. a) Temperature dependent T_M measurements of the ^1H @POSS cage system (depicted in the upper left corner) in different matrices (protiated solvents, deuterated solvents and pristine powder). b) Temperature dependent ENDOR measurements at the ^1H Larmor frequency indicating structural insight in the pristine powder.

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Direct observation of chirality-induced spin selectivity in electron donor–acceptor molecules

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The role of chirality in determining the spin dynamics of photoinduced electron transfer in donor-acceptor molecules remains an open question. Although chirality-induced spin selectivity (CISS) has been demonstrated in molecules bound to substrates, experimental information about whether this process influences spin dynamics in the molecules themselves is lacking. We have demonstrated that time-resolved electron paramagnetic resonance spectroscopy can be used to show that CISS strongly influences the spin dynamics of isolated covalent donor-chiral bridge-acceptor (D-B γ -A) molecules in which selective photoexcitation of D (A) is followed by two rapid, sequential electron-transfer (hole transfer) events to yield D $\bullet+$ -B γ -A $\bullet-$. Exploiting this phenomenon affords the possibility of using chiral molecular building blocks to control electron spin states in quantum information applications^[1].

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Optical Spin Hyperpolarization in Chromophore-Radical Molecules for Dynamic Nuclear Polarization and Quantum Information Science

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Nuclear Magnetic Resonance (NMR) is one of the most information-rich techniques for advanced molecular analysis and has potential for advancing Quantum Information Science (QIS). However, NMR-based tools suffer from poor signal sensitivity. Hence, hyperpolarization of electron spins by optical excitation and subsequent transfer to nuclear spins is of enormous interest since this approach has the potential to transfer tens of % optical polarization to nuclear spins whose thermal polarization at low magnetic field and physiological temperature is of the order of ppm. The best-known current systems that have shown promise in optical dynamic nuclear polarization (DNP) are diamond NV-center¹ and molecular triplets² that can achieve enhancement values of several orders of magnitudes larger than thermal equilibrium at room temperature, but these systems are not readily tunable.

This project focuses on testing chromophore-radical (CR) molecules for optical DNP and QIS applications. After a selective laser excitation to a singlet state, the chromophore undergoes enhanced intersystem crossing to a triplet state. This triplet and the radical spin doublet can couple strongly or weakly by exchange. The quartet state in the strong coupling case is a promising candidate for a qudit. Nevertheless, the selective relaxation from the excited state to the radical ground state is known to generate electron spin polarization of the radical for both strong and weak coupling cases^{3,4}. Importantly, many CR systems have been shown to give rise to strong electron spin polarization in solution even at room temperature and is not orientation dependent. Furthermore, a non-abundant atom in the molecule can be hyperpolarized to serve as a quantum memory unit (see Figure 2).

However, there are many critical open questions to realize an efficient transfer of polarization from light to electron spins to other nuclei. This project will focus on the mechanism of electron spin polarization and nuclear spin polarization by DNP at X- and Q-band field. We are looking into the effect of molecular motion and orientation on the electron spin T1, and T2 effects, and their impact on the efficiency of optical polarization of the radical and nuclear spin hyperpolarization by DNP. We are also examining the polarization transfer pathway from radical pairs to electron spins to nuclear spins within the CR and outside of CR to analyte nuclei. References:

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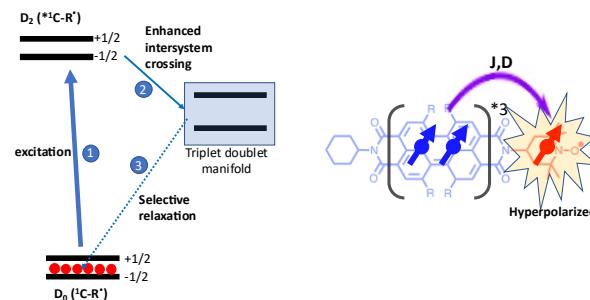


Figure 1. Optical hyperpolarization of the radical. The chromophore undergoes ultrafast EISC to a triplet and interacts with the radical. The selective relaxation gives rise to a hyperpolarized radical

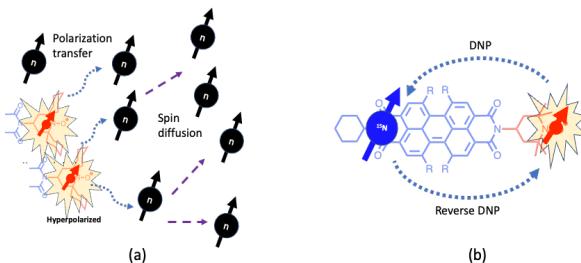


Figure 2. The potential applications of CR systems in (a) DNP: the hyperpolarized electron can be used to polarize nearby nuclei in the matrix and in (b) Quantum Information: a nucleus can be selectively placed in the CR system for polarization transfer to act as a long-lived quantum computing/memory unit.

Condensing magnetic resonance spectroscopy theories with VIKING web suite

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The study of phenomena within the topic of spin chemistry (e.g. spin-correlated radical pairs^[1]) relies on a plethora of magnetic resonance experiments (see e.g., NMR, EPR, photo-CIDNP, DEER, etc.)^[2-4]. Theoretical interpretations of these experiments are becoming difficult due to the number of different employed techniques and complexity of the underlying studied system. Hence, in this work we present a generalized computational toolkit for experimental and theoretical investigations that roots upon spin-dynamics implemented in the MolSpin^[5,6] program. Two different propagation approaches for the density matrix calculation are included, namely: direct propagation to infinite time and numerical propagation on a time grid towards desired total time. These approaches make it possible to simulate different commonly employed techniques such as continuous wave or pulse sequence programmed resonance experiments. To allow the simulations of a wide range of experiments, ranging from magnetic resonance to quantum computing, we implemented a possibility to study spin dynamics of arbitrary chemical systems in the presences of magnetic pulse sequence perturbations. Furthermore, the employed methodology allows for the consideration of specific states, manually chosen state mixtures and temperature-dependent ensembles. The developed spectroscopy module is made available in the VIKING^[7] online platform which allows anyone without programming experience to access the new features and carry out simulations for the experiments of interest.

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Evolution of spin polarization in time-resolved EPR studies reveals insights into the photovoltaic mechanism of organic solar cells

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Organic photovoltaics (OPVs) have shown a remarkable rise in efficiencies over the last decade, recently reaching 20%.^[1] This progress has been driven by pairing organic polymer electron donors with organic non-fullerene electron acceptors (NFAs), a significant improvement on earlier fullerene acceptors. Differences in performance between donor:acceptor blends are not yet fully understood and the exact photovoltaic mechanism, including the pathways of free charge generation, is still debated in the literature.^[2]

The photoexcited charge-separated (CS) state and the separated charges, key players in energy conversion, contain unpaired electron spins and so can be selectively probed by time-resolved EPR (TREPR). We have carried out a comprehensive TREPR study on a series of OPV blends, investigating the effects of temperature, laser fluence and microwave frequency, in order to examine correlations of the nature and dynamics of photogenerated states with power conversion efficiency. PM6:Y6 and PBDB-T:ITIC, NFAs with efficiencies of 16% and 11%, were considered, alongside their fullerene analogues, PM6:PCBM and PBDB-T:PCBM (both 8%), and compared to the previously well-characterized P3HT:PCBM (6%).

All photovoltaic blends show a characteristic singlet-born CS state at early times. Simulation of both X- and Q-band spectra revealed a distribution of exchange and dipolar couplings and orientations for all donor:acceptor pairs – the distributions narrowing for the NFAs. At long times after laser excitation, the spin polarization evolves to a predominantly absorptive signal. The intensity of this contribution relative to the early-time CS state is more pronounced for the NFA blends and increases with laser fluence. Modelling of the full TREPR surface as a decaying singlet-born CS state is unable to reproduce the experimental results; an equilibrium between separated charges and the CS state must also be included.

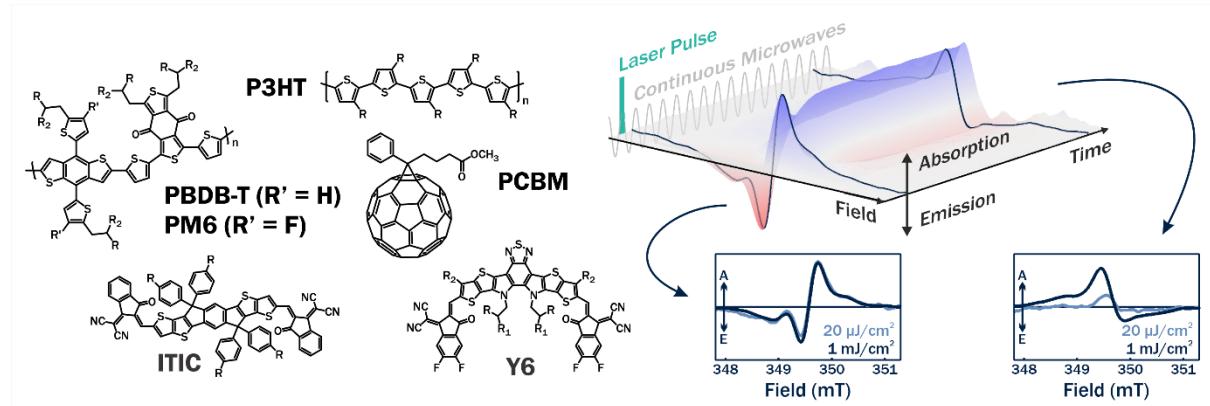


Figure 1. Molecular structures of the donors and acceptors considered, and TREPR spectrum of PBDB-T:ITIC, with spectra extracted at short and long times after photoexcitation.

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Radical exciton quenching in solid-state films of TTM-1Cz

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Luminescent organic radicals with unpaired electron ground states are expanding the range of photophysics and spin properties of molecular materials for optoelectronics. TTM-1Cz is the ‘fruitfly’ luminescent radical displaying excellent optical properties from transitions between doublet ground and excited states: leading to exploitation in light absorption to initiate photon upconversion¹ and high efficiency organic light-emitting diodes² (OLEDs). However the implementation of radicals such as TTM-1Cz in devices is limited by diminished properties on translation from solution to solid-state films. This has been attributed to concentration quenching without any mechanistic studies that can inform better molecular design of radicals.

Here we present an experiment and theoretical study that investigates radical concentration effects in TTM-1Cz : polymer films by optical spectroscopy and exciton modelling. This system provides a testbed for understanding the effects of exciton diffusion, intermolecular interactions and host environment effects on radical exciton dynamics. Understanding the cause of limitations for the current generation of triphenylmethyl radicals in their solid-state optical properties could enable future implementation of neat radical films for applications beyond OLEDs in optoelectronics and new energy technologies.

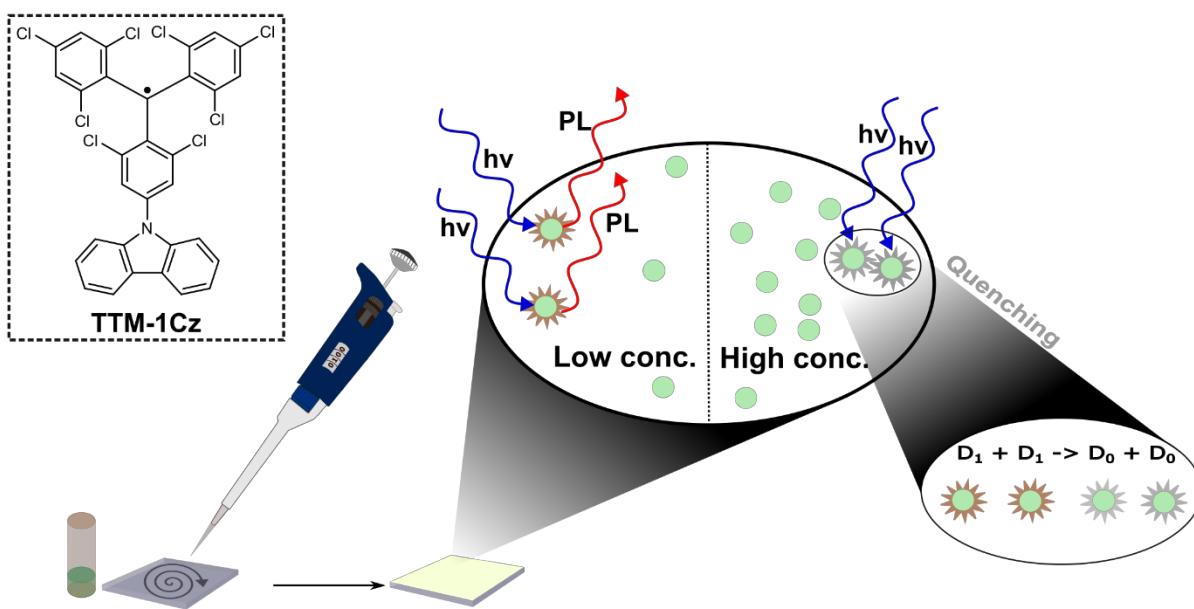


Figure 1: The structure of TTM-1Cz & and the experimental process of the study with concentration quenching effects.

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Funding acknowledgements: Royal Society (URF/R1/201300)

Electron and Nuclear Spin Interactions in Porphyrin Radical Anions

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Supramolecular electronics is an emerging field that investigates the effects of non-covalent interactions on the conductance of single-molecules.^[1] Chains of π -conjugated porphyrins have previously been shown to function as molecular wires,^[2] making them interesting for applications in spintronics and photovoltaic devices. In addition, porphyrins are a well-established building block in supramolecular chemistry and are therefore well-suited to study structure-property relationships.

Initially, we studied the delocalization of spin density in individual radical anions of butadiyne-linked porphyrin oligomers of different lengths. These display coherent spin delocalization over 3-4 porphyrin units as shown by both optical spectroscopy and low temperature ENDOR spectroscopy (Fig. 2a). Room temperature CW EPR measurements along with ab-initio molecular dynamics simulations show that at higher temperature dynamical processes lead to time averaged delocalization of spin density over at least eight porphyrin units.

In addition, porphyrin ladder complexes offer an excellent way to hold two spin centres in a well-defined structure (shown in Fig. 1). PENANUT experiments have been used to confirm the presence of a triplet species (Fig. 2b). These findings are expected to inform the future design of (supra-)molecular electronic devices.

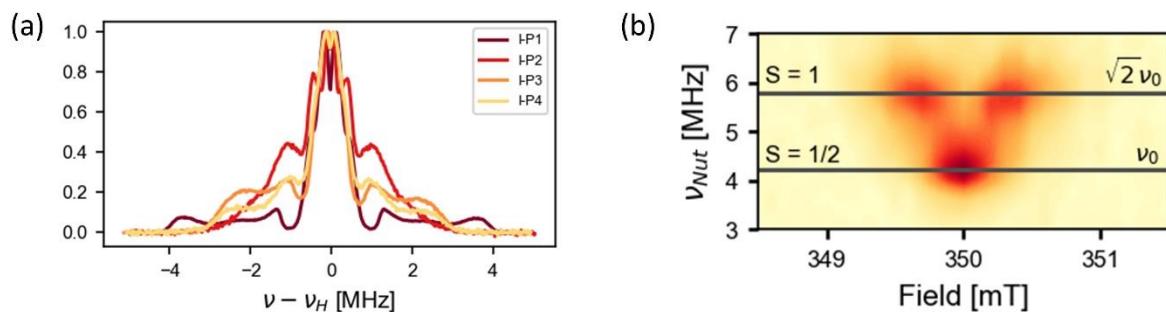


Figure 2: (a) ^1H ENDOR spectra of $I\text{-P}N$ radical anions ($N = 1\text{-}4$). (b) PEANUT field sweep of $(I\text{-P}3)_2\bullet(\text{bipy})_3$ after Fourier transform.

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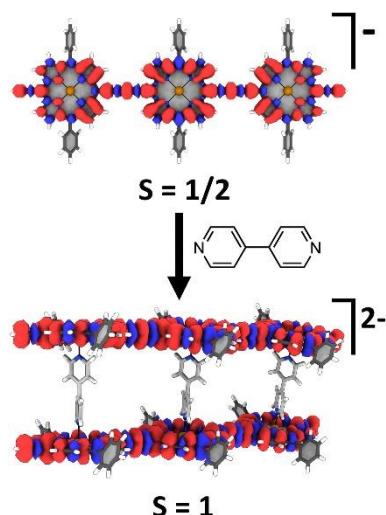


Figure 1: Porphyrin radical anions form ladder complexes

Spin Physics of a Photoexcited Gadolinium Complex: Quantum Photo-switching by EPR Spectroscopy

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The electronic and magnetic properties of lanthanide (Ln) elements have been widely used in both medicine and industry, such as in magnetic resonance imaging (MRI) contrast agents, superconductors, and laser crystals. [1-3]

The contracted nature of the 4f-orbitals and the Laporte-forbidden nature of 4f-4f transitions allow lanthanide ions to have non-reactive, high spin species which have both long lifetimes in their excited states and long relaxation times. Lanthanide complexes, therefore, have been a key target in developing molecular systems capable of quantum memory storage.[4] Gadolinium (III), in particular, could be useful as it has the highest ground spin state, $S = 7/2$, for a single atom and no net orbital angular momentum. However, unlike other lanthanides, generating photoexcited states is typically challenging due to the very large energy gap, around 32000 cm^{-1} , to the next excited state and low molar absorption coefficient. [5,6] Hence, new ways of generating excited states and manipulating the spin state of gadolinium, without using high energy excitation, could prove useful for developments in quantum information theory (QIT).

By utilising a DO3A cage, two Ln^{III} ions, Gd^{III} ($4f^7$) and Lu^{III} ($4f^{14}$), were directly bonded to an aryl chromophore as seen in Figure 1. Photoexcitation of the chromophore was able to perturb the electronic states of the Gd^{III} ion. The nature, formation and relaxation of the resulting Gd^{III} excited states were then investigated via a variety of optical and magnetic resonance techniques.

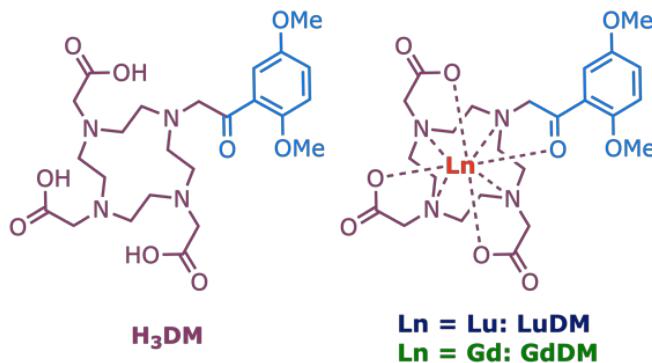


Figure 1: A range of complexes studied. The DO3A cage (purple) allows for a stable lanthanide (red) coordination environment with a chromophore (blue) directly bonded to the lanthanide allowing for effective communication between the lanthanide and chromophore excited states.

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Ab initio study of electron spin-lattice relaxation of triplet oligoacenes

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Introduction

Photo-excited triplet molecules are one of the attractive systems in spin chemistry because they can achieve high spin polarization even under mild conditions and can be applied to recently emerging quantum technologies such as dynamic nuclear polarization and quantum computing. So far, we have performed ab initio calculations of the D tensor and polarization ratio of the novel polarizing agents to evaluate their performance^[1,2]. On the other hands, spin-lattice relaxation (SLR) time is also important for them, however, there are still no examples of evaluating the SLR of such important triplet organic molecules in an ab initio manner. Therefore, we conducted ab initio spin dynamics calculations for triplet oligoacenes to investigate the relationship between molecular structure and SLR time.

Method and Results

The following spin Hamiltonians were used for describing triplet molecules.

$$\hat{H}_S = \mu_B g_e B_z \hat{S}_z + \hat{\mathbf{S}} \mathbf{D}(\Omega) \hat{\mathbf{S}}, \quad \hat{H}_{S-B} = \sum_{\alpha} \left(\hat{\mathbf{S}} \frac{d\mathbf{D}(\Omega)}{dQ_{\alpha}} \hat{\mathbf{S}} \right) \hat{Q}_{\alpha}$$

Hyperfine and spin-orbit couplings were not considered because they are much smaller than spin-spin coupling in triplet oligoacenes. Then, spin dynamics can be described by the Redfield equation using the following spin-phonon coupling strength and spectral density^[3].

$$V_{ab}^{\alpha} = \left\langle a \left| \hat{\mathbf{S}} \frac{d\mathbf{D}(\Omega)}{dQ_{\alpha}} \hat{\mathbf{S}} \right| b \right\rangle, \quad G(\omega_{ab}, \omega_{\alpha}) = \frac{\Delta_{\alpha} n_{\alpha}}{\Delta_{\alpha}^2 + \hbar^2(\omega_{ab} + \omega_{\alpha})^2} + \frac{\Delta_{\alpha}(n_{\alpha} + 1)}{\Delta_{\alpha}^2 + \hbar^2(\omega_{ab} - \omega_{\alpha})^2}$$

where the phonons were assumed to be always in thermal equilibrium because the timescale of the phonon relaxation is much faster than the SLR. The phonon frequencies and D tensors, which are parameters of this model, were determined by quantum chemical calculations.

The relative magnitudes of the transition rates between each sublevel of pentacene obtained from the calculations qualitatively matched the experimental results measured in the p-terphenyl crystal (**Table 1**). Additionally, the vibrational mode with the largest contribution to the one-phonon relaxation was found to be an out-of-plane distortion at 141 cm^{-1} with b_{3g} symmetry.

	Calc.	Exp. ^[4]
w_{XY} (ms ⁻¹)	0.33	4
w_{YZ} (ms ⁻¹)	2.30	22
w_{XZ} (ms ⁻¹)	0.46	11

Table 1. Transition rate constants between each sublevel of pentacene at zero magnetic field and room temperature. Phonon frequencies and D tensors were calculated at TD LC-BLYP($\mu=0.15$)/def2-TZVP and CASSCF(8e,8o)/cc-pVQZ level, respectively.

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Orientation-Independent Triplet DNP with Fullerene-Based Polarizing Agents

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Triplet-DNP that utilizes photo-excited triplet electrons can achieve nuclear hyperpolarization at high temperature because high electron spin polarization between triplet sublevels is maintained independent of temperature due to spin-selective intersystem crossing ^[1]. However, to achieve over 10% nuclear polarization, pentacene-doped single crystals had to be precisely oriented in a magnetic field to focus electron spin resonance (ESR) within a narrow field range for effective polarization transfer, which was not practical for real-world applications ^[2]. Here we present new fullerene-based polarizing agents showing sharp ESR spectra due to small dipole interactions between electron spins, frees the polarizing agent from orientation-dependent constraints. While fullerenes have not been used as polarizing agents because of the short spin-lattice relaxation time of triplet electron spins (T_{1e}) due to pseudo-rotation, we found that the T_{1e} significantly extended by chemical modifications (Figure 1a)). We achieved a practical ^1H polarization of 14.2% by triplet-DNP even with the randomly oriented polarizing agents (Figure 1b)).

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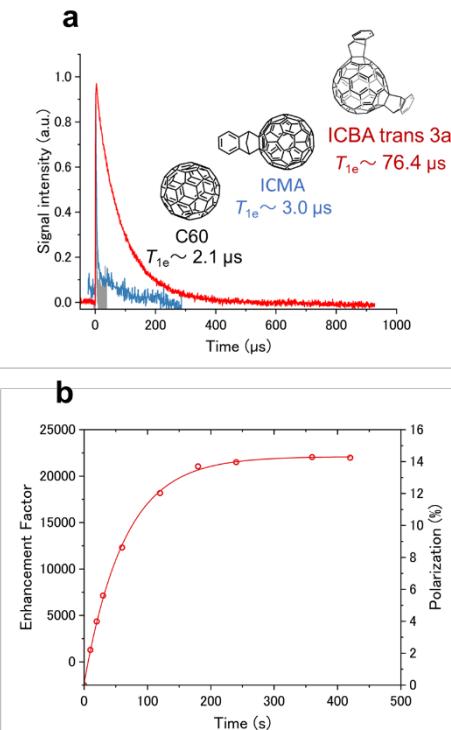


Figure 1. a) ESR signal decay of C60, ICMA and ICBA trans-3a 0.05 mol% doped in *o*-terphenyl at 140 K. b) Build-up curve of ^1H NMR signal intensity of partially deuterated OTP (OTP:[D14]OTP= 10:90wt%) doped with 0.05 mol% of ICBA trans-3a.

Time-resolved EPR study of intramolecular exciton hopping contributing to triplet-triplet annihilation-based photon upconversion

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[Introduction] Triplet-triplet annihilation-based photon upconversion (TTA-UC) is a process that can convert even low intensity and incoherent photons into a higher energy photon. TTA-UC is expected to improve the efficiency of photovoltaics and photocatalysis using sunlight as light source, as well as for medical applications such as bioimaging. In this study, we employed TAB consisting of three anthracenes linked via boron in a 3D orthogonal relationship, as a TTA material. We revealed intramolecular triplet exciton hopping mechanism in TAB molecule (Fig. 1) using time-resolved electron paramagnetic resonance (TR-EPR) and clarified how triplet exciton vibronic dynamics in TTA materials affects TTA-UC process, which requires intermolecular collisions of the two triplet excitons.

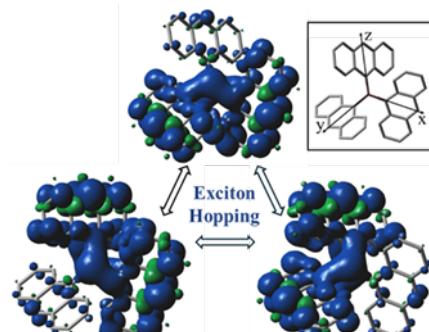


Figure 1. Intramolecular triplet exciton hopping in TAB molecule.

[Results and Discussion] TR-EPR measurements were performed at room temperature on samples of TAB and the triplet sensitizer, PtOEP, dissolved in solvents of different viscosities; mixture of toluene <T> and liquid paraffin <P> in three volume ratios. The Liouville equation analysis of the spectra shapes considers that 3D orientation of triplet excitons relative to an external magnetic field changes rapidly due to pseudo-rotation caused by intramolecular triplet exciton hopping between three anthracenes (Fig. 1). [1] The results show that in T:P=1:1 solvent (lowest viscosity solvent), triplet excitons hop between each anthracene moiety rapidly, causing sharp EPR spectrum due to motional narrowing in the spin-spin dipole interaction (Fig. 2 (a)). Furthermore, in higher viscosity solvents (T:P=1:9,1:19), the broad triplet excitons signals emerged, indicating that this hopping is controlled by the viscosity (Fig. 2 (b), (c)). In addition, we discovered that the intramolecular migration of triplet excitons due to this hopping also enhances the rate of TTA (k_{TTA}) using time-resolved luminescence measurements. This indicates that the vibronic trimer design is beneficial for increasing effective collisions between triplet excitons and improving TTA-UC efficiency.

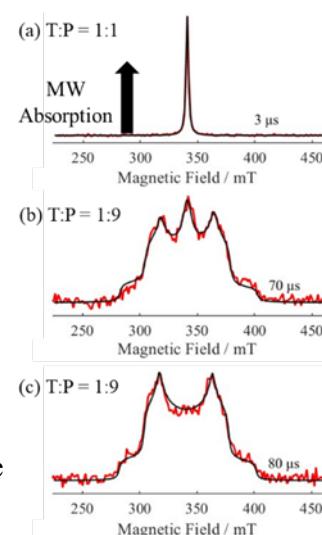


Figure 2. TR-EPR spectra of PtOEP/TAB system in solvents of different viscosities.

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B1-01

Quantum theory of a potential biological magnetic field sensor: radical pair mechanism in flavin adenine dinucleotide biradicals

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Abstract Quantum biology is an exciting and broad field that tries to explain biological phenomena that cannot be treated via classical approaches. One interesting area of this blooming field is magnetoreception, the ability of biological systems to sense and use Earth's magnetic field for navigation and other functions [1]. It is important to have a deep understanding of the mechanisms behind magnetoreception both for its fundamental interest and because of potential technological applications such as bio-inspired magnetosensors. Several models have been developed to explain magnetoreception in biological systems, and the most prominent one among them is radical-pair mechanism (RPM) [2], which is based on the quantum dynamics of electron and nuclear spins in pairs of radical molecules. While Cryptochrome has historically been the main candidate for RPM magnetoreception, recent experimental results suggest that flavin adenine dinucleotide (FAD) alone might also act as a biological magnetosensor [3].

For further evaluation of these results, a detailed theoretical model for the observed magnetic field effects (MFEs) on FAD is needed. Previous models of FAD's photochemistry under magnetic fields were based on semi-classical approaches, which could only describe the two extreme cases of high and low magnetic fields [4, 5]. Our study addresses this gap by developing a fully quantum model that predicts the MFEs on FAD for all magnetic field magnitudes. Our quantum theoretical model for the RPM in FAD incorporates Zeeman, hyperfine, exchange, and dipole-dipole interactions. We performed molecular dynamics simulations to determine the dynamic distances between radicals in FAD, which we then integrated into a quantum master equation to calculate the spin dynamics under different magnitudes of magnetic fields. Our theoretical results of the MFEs on the photochemistry of FAD are consistent with experimental results on the transient absorption of this molecule in the absence and presence of external magnetic field.

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A Quantum Inclination Compass - Elucidating the Inner Workings of Avian Magnetoreception with Confocal Microscopy

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The molecular origins of animals' ability to sense the geomagnetic field remain one of the biggest open questions in biology. For migratory songbirds, the leading hypothesis relies on the quantum spin dynamics of light-induced radical pairs in the putative magnetoreceptor protein, cryptochrome 4a^[1]. Decades of behavioural studies show a correlation between anomalies in Earth's magnetic field and a disruption of pigeons' (*C. livia*) navigational system^[2]. For European robins, the navigational ability appears to depend exclusively on blue and green light^[3] and relies on sensing the geomagnetic field inclination^[4].

Magnetic fields can affect the product distribution, rate, or yield of chemical reactions which proceed via radical pair intermediates^[1]. Absorption-based spectroscopic techniques have successfully unravelled the underlying magnetic field-sensitive photochemistry of cryptochromes in solution^[5]. However, if cryptochromes *in vivo* were to tumble freely in the cytoplasm, the stochastic motion would average any direction-sensitive magnetic field response to zero. Instead, association with the cytoskeleton or cell membranes is likely to provide the immobile framework needed for a number of partially aligned cryptochromes, whose coordinated response presumably boosts the sensitivity of the avian compass and signals the magnetic field inclination to the bird^[1]. Following the development of confocal microscopy for the study of mT-strength magnetic field effects^[6], we now demonstrate *anisotropic* magnetic field effects in immobilised avian cryptochrome 4a for the first time. In this work, we show that the fluorescence intensity of single crystals of *C. livia* cryptochrome 4a is modulated by the direction of an applied magnetic field of fixed magnitude (16 mT), establishing cryptochrome fit for purpose as a chemical inclination compass. The findings are rationalised in terms of photoselection, the spatial orientation of crystals down to the arrangement of individual residues and flavin co-factors within the unit cell, and corroborate the viability of radical pair-based cryptochrome-mediated magnetoreception.

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Supported by the European Research Council under the European Union's Horizon 2020 Research and innovation programme, Grant Agreement No. 810002, Synergy Grant: 'QuantumBirds'.

B1-03

Cavity ring-down measurements by continuous pulse trains for Biomolecules

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Radical pair reactions and magnetic field effects (MFEs) of photoreceptor proteins such as cryptochromes[1] have attracted attention. However, measuring these using transient absorption is difficult, especially on the precious biological samples. Cavity ringdown spectroscopy (CRDS)[2-3] can measure the transient absorption (TA) of the low concentration photochemical intermediates with high sensitivity and quantitative accuracy by amplifying the effective optical path length using a light cavity. However, in the pump-probe type CRDS experiment, multiple excitations of the sample are required to obtain time-resolved data. This feature is a disadvantage when compared with the typical TA setup using a CW probe light source. The SCRD instrument developed in our laboratory can continuously measure a large number of TAs in the time domain by using a supercontinuum (SC) light source as the probe beam. This is because the supercontinuum light source used in this study is a train of pulses fired at precise intervals, with each pulse ringing in the optical cavity and its decay reflecting the optical TA of the sample at each time. It is therefore possible to obtain a time dependence of the TA with a single shot of excitation light. In practice, it is possible to measure MFE on the order of 10^{-5} with a small number of laser flash photolysis.

Figure 1 shows the results of MFE using SCRDS of 50 μM FMN and 200 μM HEWL system by changing the external magnetic field. By averaging the MFE over the range of 10 μs to 90 μs , the measurement error was reduced to $\pm 0.25\%$ with 200 shots each magnetic field. The SC source is the broad band white light, so it is also suitable for measuring the wavelength dependence of the time-dependent transient absorption. Figure 2 shows the results of transient absorption measurements at wavelengths from 500 to 700 nm of the 200 μM FMN and 200 μM HEWL system. The time-resolved TA spectrum can be obtained with only 4000 laser shots. Further improvement using the multi-colour detection system would save more than 8 times the number of excitations.

In conclusion, SCRDS enables multifaceted measurements such as time-varying TA spectrum measurement and MFE with a small number of excitation light irradiations.

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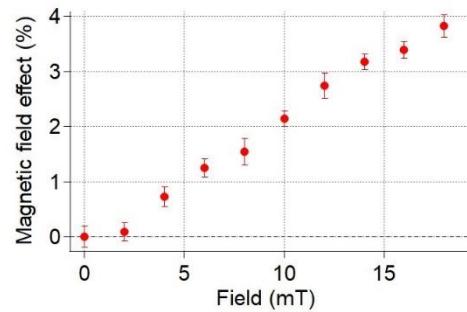


Figure 1 : Magnetic Field Effect using SCRDS. 200 shots averaged per points.

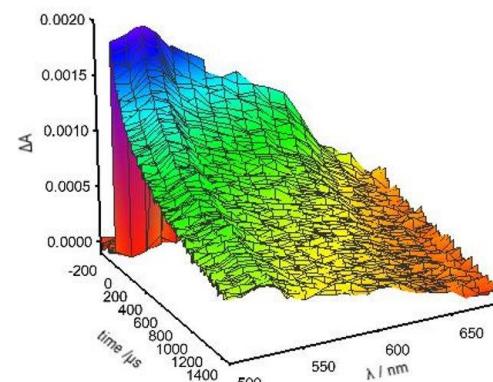


Figure 2 : Time-resolved transient absorption spectrum. 20 nm bandwidth, 10 nm step, 200 shots per step

Exploring the Role of a Tyrosine Radical in Avian Cryptochromes

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It has been known for some time that many animals use the geomagnetic field to aid in navigation. In particular, it has been shown that night-migratory songbirds have this magnetic sense^[1] and it is located in the eyes, but only activated under light of certain wavelengths^[2]. The blue-light absorbing flavoprotein, cryptochrome (Cry4a), has emerged as the most likely magnetoreceptor^[3] given its presence in avian retinal cells and the fact that it exhibits magnetic field effects (MFEs) *in vitro*^[4].

The magnetic sensitivity of the cryptochrome arises from a photo-induced, spin-correlated radical pair formed via electron transfer along four tryptophan (W) residues^[3]. In this low exchange regime, the singlet and triplet states are not stationary states of the total Hamiltonian and undergo hyperfine-driven coherent interconversion which is sensitive to external magnetic fields. Since each spin state has a different fate, this external field can be transmitted by the signalling state of the protein.

We report a spectroscopic study of the end of the electron transfer chain that lies at the surface of the protein. In particular we focus on the role of a tyrosine (Y) residue that is highly conserved among bird species^[5]. Replacing this tyrosine for a phenylalanine (F) has a significant impact on the extent of recombination, the MFE and the identity of the radical pair in Cry4a. This raises questions about the function of this amino acid in the avian magneto-sensing pathway. We utilise cavity-enhanced spectroscopy and point mutations in chicken Cry4a to explore the impact of the tyrosine residue on the radical pair photochemistry, its role in the protein and its interaction with neighbouring residues.

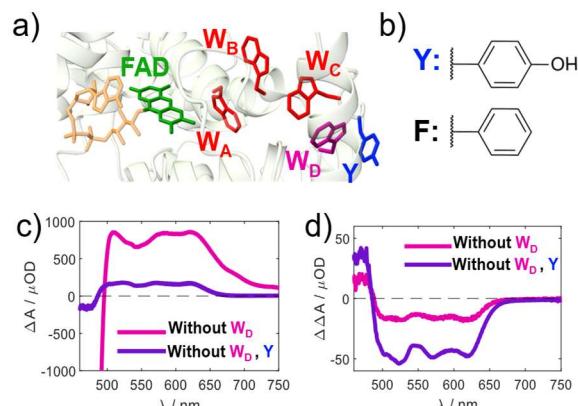


Figure 1. a) Tertiary structure of Cry4a with key residues highlighted. b) Chemical structure of tyrosine (Y), and phenylalanine (F) which is used as the non-functionalised substitute residue. c) Photo-induced absorption spectrum of GgCry4a with either W_D or both W_D and Y substituted. d) MFE subtraction of same two GgCry4a mutants.

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B1-05

Synthesis of TEMPO with a cycloalkyne group and its conjugation with an azide group via click chemistry

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DEER (Double Electron-Electron Resonance) is a powerful method for characterizing protein structures by measuring the distance between electron spins [1]. However, it requires spin labeling the protein, typically using the thiol group of a cysteine residue. By introducing a cysteine at a specific location via site-directed mutagenesis, a spin label can be attached through disulfide bonding. This method has a problem in selectivity if the protein has free cysteines where the spin label binds to both mutant and native sites. To overcome the problem, it has been developed spin label incorporating a cycloalkyne group which allows conjugation to an azide group through a biorthogonal click chemistry [2]. The azide group can be introduced into the protein by genetic code expansion or chemical modification techniques [3]. However, the method is not widely applied to the biological studies so far. Since we aimed to apply the click chemistry reactions for the proteins, we synthesized a TEMPO radical with a cycloalkyne group (Fig. 1). Conjugation of the two molecules was achieved via a strain-promoted azidoalkyne cycloaddition (SPAAC) reaction (Fig. 2).

Figure 1 shows the synthetic pathway of the spin-labeled compounds [4]. The spin label (product 6) was synthesized in five steps from cyclooctane. To evaluate whether product 6 functions as a spin label, a 4-azide TEMPO was conjugated (to product 6) via the SPAAC reaction. ESR spectra confirmed successful synthesis of the desired molecule by the presence of a biradical.

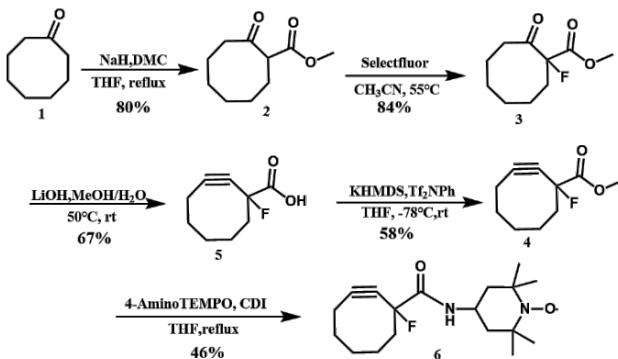


Figure 1. Synthesize scheme of the spin label

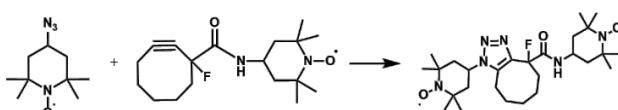


Figure 2. SPAAC reaction of the spin label with 4-azide TEMPO

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Sensitive Detection of Magnetic Field Effects in Avian Cryptochromes

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Certain avian species harness the Earth's magnetic field through magnetoreception to navigate during long-range migration. While the phenomenon of avian migration is fairly well understood, the underlying biophysical mechanisms remain disputed, offering an intriguing area for research.

The radical pair mechanism (RPM), proposed by Schulten *et al.*¹, suggests that spin-correlated radical pairs could act as a biological compass. The RPM and behavioural studies, indicating that avian magnetoreception depends on the wavelength of light birds are exposed to, have led to the hypothesis that photosensitive proteins called cryptochromes, located within the retina of migratory birds, serve as the source of magnetoreception.

In Oxford we have developed a range of optical cavity-based techniques^{2,3} with which to characterise the small absorbance changes which typically signify magnetic field effects in proteins. Each technique has its own strengths and limitations. Cavity ring-down spectroscopy is a cavity pump-probe technique with sub- μ s time resolution but limited to single wavelengths. By contrast, broadband cavity enhanced absorption spectroscopy (BBCEAS) combines full visible spectral coverage with high sensitivity (absorbance $\sim \mu$ OD) but at the expense of temporal resolution, limiting it to detection of long-lived species.

Here, we report progress towards combining the principal attributes of BBCEAS and CRDS into a single instrument providing more comprehensive characterisation of magnetically sensitive photochemistry in cryptochromes in much reduced experimental time.

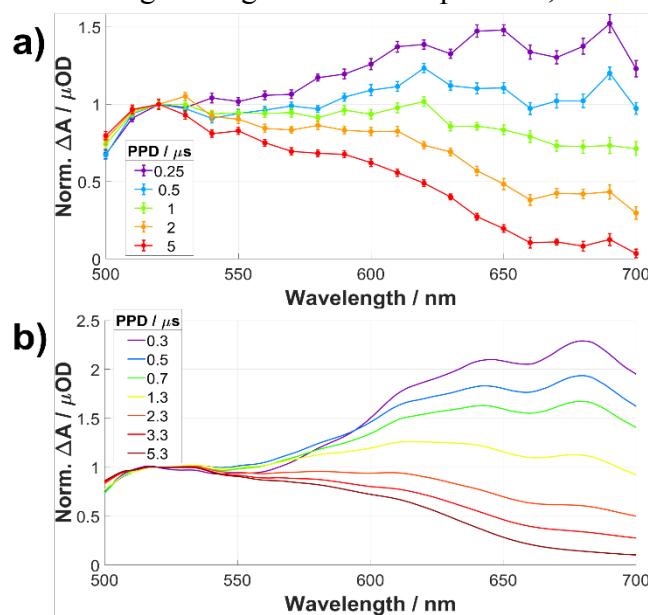


Figure 1: FMN HEWL ΔA spectra at various pump-probe delay times, illustrating the formation of photogenerated species using a) CRDS and b) a novel cavity-based technique. Unlike CRDS, which necessitates separate acquisitions at each wavelength with recovery periods in between, our new technique can probe the entire spectrum with sub-nanometer resolution in a single acquisition.

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Generation and transfer of long-lived electron spin polarization in weakly-coupled peptide bridged chromophore-radical conjugates

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A new electron spin hyperpolarization mechanism was recently observed by Di Valentin *et al.* in a weakly-coupled radical-triplet spin-system, where the triplet state precursor and the radical are held at a fixed distance.^[1] The observed transfer of electron spin polarization from the photoexcited porphyrin triplet to the radical probe was ascribed to a new hyperpolarization mechanism relying on the interplay between the dynamic Jahn-Teller effect and the dipolar coupling.^[2]

In the weakly-coupled regime, electron spin polarization transfer can have a major impact on the development of next-generation magnetic resonance techniques as the use of spin polarized stable radicals could offer increased sensitivity in both electron and nuclear magnetic resonances.^[3]

The process of hyperpolarization of nitroxide radicals weakly coupled to photoexcited chromophores was further investigated by Electron Paramagnetic Resonance (EPR) spectroscopy on several model systems. A bis-labelled template peptide (Figure 1a) was designed to connect the nitroxide radical, the artificial amino acid known as TOAC, to either ZnTPP, a I₂-BODIPY chromophore derivative or erythrosin B within a wide range of distances. Both dynamic Jahn-Teller effects and the breakdown of the high-field approximation were examined demonstrating that different mechanisms can contribute to the hyperpolarization process of weakly-coupled radicals when the dipolar interaction requirement is met. Weakly-coupled porphyrin-radical conjugates exhibited long-lasting electron spin polarization, persisting for approximately 60 ms at the liquid nitrogen temperature (Figure 1b).

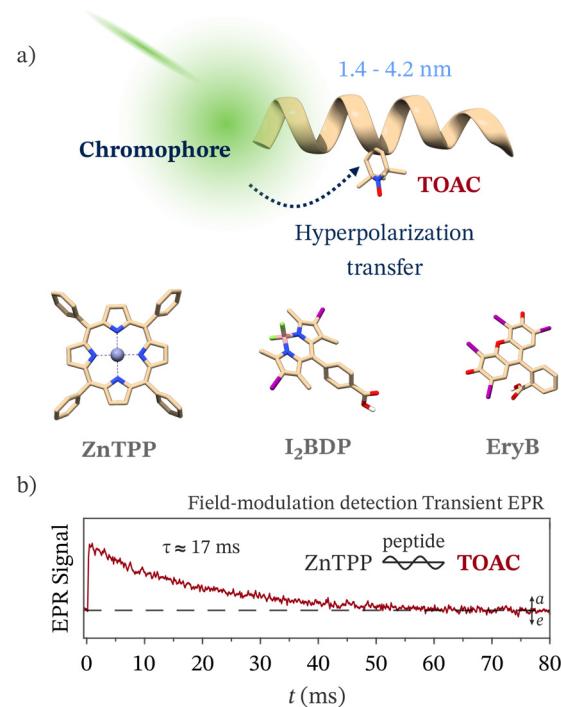


Figure 1. a) Illustration of the investigated molecular structures and chromophores. b) Field modulation detection Transient EPR of a porphyrin-radical conjugate recorded at 80 K.

Figure 1 illustrates the experimental setup and results. The top part (a) shows the molecular structures of ZnTPP, I₂BDP, and EryB, each linked to a TOAC radical via a peptide bridge. The bottom part (b) shows a field-modulation detection Transient EPR spectrum recorded at 80 K. The signal decays over time, with a characteristic decay time constant $\tau \approx 17$ ms. The plot also shows the ZnTPP, peptide, and TOAC components of the conjugate.

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B1-08

Biomimetic dyads studied by Solid State photo-CIDNP NMR

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) enhances NMR signal intensities by triggering photochemical reactions that disrupt the nuclear spin system from its Boltzmann equilibrium.

Since its discovery in solid-state systems in 1994, photo-CIDNP has been observed in various photosynthetic reaction centers using magic angle spinning solid-state NMR. The photo-CIDNP effect in solids arises from a combination of mechanisms, including three-spin mixing (TSM), differential relaxation (DR), and differential decay (DD). These mechanisms facilitate the transfer of electron spin polarization from the initial state of radical pair to the nuclei via hyperfine interactions. However, fully understanding these processes remains an active research area.

This study aims to thoroughly investigate the phenomenon of photo-CIDNP in a solid state molecular system, focusing on the interaction between electronic and nuclear spins. We use specially designed synthetic dyads with a polyproline type II (PPII) helical structure. PPII helices are abundant in nature, forming the main component of collagen and being present in many globular proteins. Given the successful demonstration of the photo-CIDNP effect in flavoproteins, we hypothesize that these synthetic dyads, which incorporate a flavin group, may also exhibit this effect. These dyads feature donor-acceptor distances ranging from 3 to 18 Å, with tryptophan or tyrosine as donors and the flavin group as the acceptor. We are also investigating the impact of different spatial orientations. The initial series of synthetic dyads has been synthesized and is undergoing theoretical and experimental analysis.

During the research, it was discovered that a helical structure of polyproline forms when at least six proline residues are present in a dyad. By now the photo-CIDNP signal was successfully obtained in our liquid-state NMR experiments. The next step involves conducting experiments on the same dyad samples to observe the photo-CIDNP effect in solid-state NMR. Additionally, an experiment is planned to study the dependence of signal intensity on the length of the polyproline chain in the dyad.

B1-09

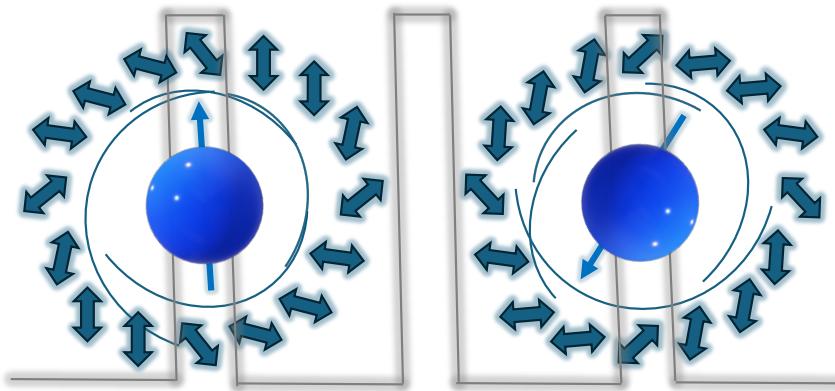
Engineering the uncontrollable in radical pairs: Controlling noise via optimal control to boost compass sensitivity

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Crucial to the realization of various quantum technologies, ranging from gate generation in quantum computation, to the laser control of chemical reactions, is the ability to control the dynamics of open quantum systems^[1]. While dissipative effects are generally seen as obstacles to surmount for controlling such complex quantum systems, curiously, in some cases they could in principle be harnessed as a possible control knob. For biradical spin systems, dissipative



effects like electron spin relaxation and spin decoherence have been shown to boost magnetometric sensitivity^[2]. This opens the door to the potential incoherent modulation of such dissipative effects (in other words, by engineering the environment through tuning the noise degrees of freedom) via optimal control. Exploring this exciting possibility theoretically poses significant challenges, since techniques such as gradient-based optimization^[3] incorporating the full Liouville space description of open systems dynamics becomes computationally intractable for realistic systems descriptions. Thus, we explore a numerically feasible Pontryagin Maximum Principle based control engineering approach instead. We adapt our method to study simple radical pair systems implicated in spin sensitive (bio-)chemical reactions, like FAD/Z, to obtain initial results investigating the potential for controlling radical pair recombination reactions via engineered environments.

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Spin relaxation in peroxy lipid radicals in a bilayer

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Spin correlation between radicals plays an important role in numerous biological processes, with spin relaxation describing the process of the correlation weakening due to interactions with the environment. An earlier study showed that magnetic field effects (MFEs) can arise from spin-correlated radicals in a model bilayer with peroxide lipid radicals^[1]. However, the coherence among radicalized lipids must be maintained for a sufficient time for MFEs of measurable strength which raises the question if such effects are truly viable in hot biological environments.

This study investigates whether MFEs persist amidst spin relaxation processes within lipid bilayers. Employing a comprehensive approach, including all-atom molecular dynamics simulations, density-functional-theory-based calculations and spin dynamics calculations utilizing Bloch–Redfield–Wangness relaxation theory, we assess the impact of spin relaxation on the observed MFEs. Building upon previous research linking spin relaxation to internal motions in plant cryptochromes^[2,3], we focus on a lipid model membrane comprising phosphatidylcholine (PC) lipids and a small number of their peroxy radicals.

Thermal motion of the peroxy lipid including rotation of the peroxide group and movement relative to the external magnetic field emerged as a crucial degree of freedom influencing subsequent spin relaxation in radicalized lipids.

The hyperfine coupling constants of nuclei near the peroxide group were calculated and used in the spin dynamics calculations. Spin relaxation effects caused by changes in the hyperfine coupling, changes in the g-tensors and the spin rotational interaction coupling to the rotation of the peroxide group were evaluated.

It was found that MFEs persist in a lipid bilayer with spin relaxation due to thermal motion. The dominant relaxation pathway was the Δg -mechanism which predominantly affects the spin dynamics at large applied magnetic fields. Furthermore, our analysis suggests the range of external magnetic field strength where the largest MFEs could be expected depending on the lifetime of the radical pair. Our investigation provides valuable insights into the efficiency of spin relaxation processes within lipid bilayers and offers a generalized outlook on spin relaxation phenomena in analogous biological and noisy environments.

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B1-11

Triplet dynamic nuclear polarization of pyruvate with bio-compatible matrix

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Triplet-DNP is a promising technique that enhances NMR intensity by transferring the polarization of the photo-excited triplet electron spins to probe nuclear spins.^[1] In particular, the tracing of the metabolic pathway of [1-¹³C] pyruvate can be utilized for MRI cancer diagnosis. Hence, the hyperpolarization of [1-¹³C] pyruvate is a critical step toward the practical use of triplet-DNP. In the previous research, we have reported the first triplet-DNP of [1-¹³C] pyruvate with a water-soluble supramolecular polarizing agent. However, achieving nuclear polarization at practical level remains challenging.^[2] The difficulty arises from the short spin-lattice relaxation time (T_1) of matrix material. In previous studies, there are few examples of biocompatible matrices that can mix with [1-¹³C] pyruvate, and their short T_1 (~46 s) cause rapid relaxation from a polarized state to a thermal equilibrium state.

In this study, we aim to develop biocompatible matrix materials which can disperse [1-¹³C] pyruvate and exhibit long T_1 (~min). We screened different types of biocompatible compounds with T_1 measurements using the saturation recovery method. Mixtures of long T_1 molecules and pyruvate were prepared by the melt quenching method. We optimized the mixing combinations and ratios, as well as the deuteration ratios, and investigated the preparation method for practical matrices. In the current stage, the polarization of photoexcited triplet electron spins in C₆₂(COOH)₄ was successfully transferred to the ¹H spins in matrices.

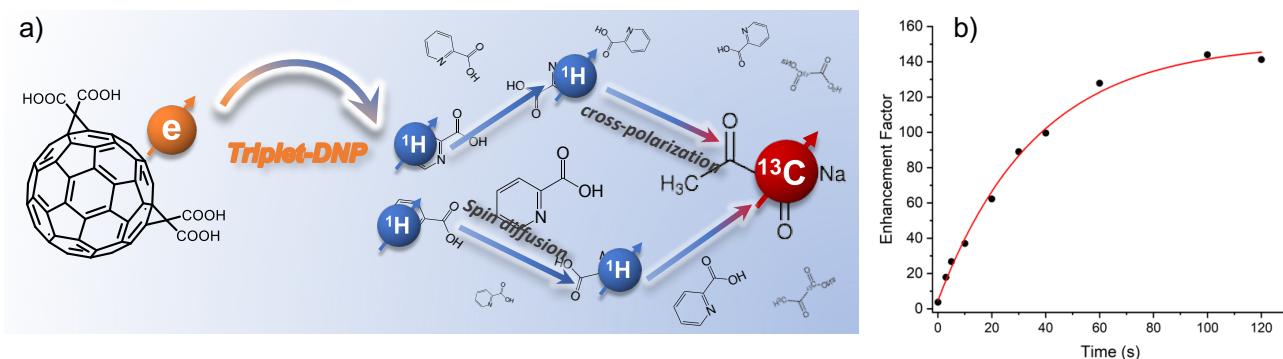


Figure 1. Illustration of triplet-DNP: a) schematic diagram of spin transfers in triplet-DNP, b) build-up curve of ¹H polarization of nicotinamide in the presence of sodium pyruvate.

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Droplet-Based Microfluidics as a Novel Method of Magnetic Field Effect Detection in Cryptochrome Magnetoreceptors Involved in Avian Navigation

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Each year, millions of migratory songbirds embark on long-distance seasonal migrations, navigating and orientating the globe with remarkable precision using the Earth's magnetic field as their guide^[1]. Studies suggest that there exists a light-driven magnetic compass located in the retinas of migratory birds, which relies on the quantum spin dynamics of photoinduced radical pairs (RPs) in the photoreceptor flavoprotein cryptochrome (Cry)^[2]. Experimental applications of magnetic fields on Cry RPs have been shown to reduce the efficiency of singlet-triplet quantum state interconversion^[3] – referred to as magnetic field effects (MFEs) – that alter the chemical yields and rate kinetics explained by the radical pair mechanism photocycle^[4].

Here, we introduce droplet-based microfluidics as a novel technique for analysing Cry flavoproteins, offering minimal sample consumption and protein encapsulation through automated, high-throughput generation of monodisperse microdroplets. By integrating this method with confocal fluorescence microscopy, we elucidate variations in Cry photoreactions under the influence of magnetic fields. By way of proof of principle, we present spectroscopic characterisation of three Cry flavoprotein model systems:

- (1) flavin adenine dinucleotide (FAD) in citric acid buffer (pH 2) to unravel the relation between continuous fluorescence MFEs and laser induced sample degradation;
- (2) flavin mononucleotide (FMN) with ascorbic acid to demonstrate the sensitivity of the experimental technique and manifestation of low field effects; and
- (3) riboflavin with tryptophan to monitor the influence that the microdroplet size reduction has on MFEs.

The findings constitute the successful development of the microdroplet fluorescence technique, and the future applications of droplet-based microfluidics will include fluorescence MFE studies on *in-vitro* Cry proteins.

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C1-01

Nuclear Spin Hyperpolarization of *cis-trans* Photoswitchable Molecules by Parahydrogen

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Over the past decade, azobenzene-based molecular photo-switches have emerged as promising control devices in chemistry, biology, and pharmacology, due to their ability to dynamically control processes with high spatiotemporal precision using light as an external stimulus, effectively altering protein activity, controlling mitosis with single-cell spatial precision, studying the biological role of specific receptors, and storing solar energy. This study introduces an innovative approach termed Photo-SABRE^[1], combining Signal Amplification by Reversible Exchange (SABRE) and parahydrogen with light irradiation at ultralow magnetic fields (400 nT) to achieve substantial nuclear spin polarization in azobenzene isomers.

We report enhancements of 23,000-fold and 9,200-fold for the *cis* and *trans* isomers of azobenzene, respectively, compared to their thermal ¹⁵N NMR signals at 9.4 T. Our results demonstrate that only *cis*-azobenzene directly acquires significant hyperpolarization from parahydrogen via coherent polarization transfer in SABRE. Reversible photoinduced *cis-trans* isomerization at ultralow magnetic fields preserves the SABRE-derived nuclear hyperpolarization of *cis*-azobenzene, subsequently hyperpolarizing *trans*-azobenzene despite its sterically hindered direct coordination with the SABRE Ir-complex (Figure 1).

This method also facilitates the hyperpolarization of the long-lived spin order of *trans*-azobenzene ¹⁵N spins, with a lifetime of about 25 minutes, greatly exceeding their relaxation times at high (10 seconds) and low (200 seconds) magnetic fields. This long-lived spin order can be detected by ¹⁵N or ¹H NMR, presenting significant advantages for various applications.

The efficiency of polarization transfer in the SABRE method is significantly influenced by temperature. We have developed an improved device for sample thermal stabilization in an ultralow magnetic field under light irradiation. The temperature dependence of ¹⁵N SABRE for both *trans* and *cis* azobenzene at various magnetic fields has been investigated. Our results demonstrate that the maximum polarization levels of ¹⁵N nuclei are achieved at 37 degrees Celsius.

Funding: This work was supported by the Russian Science Foundation (grant number #23-73-10103)

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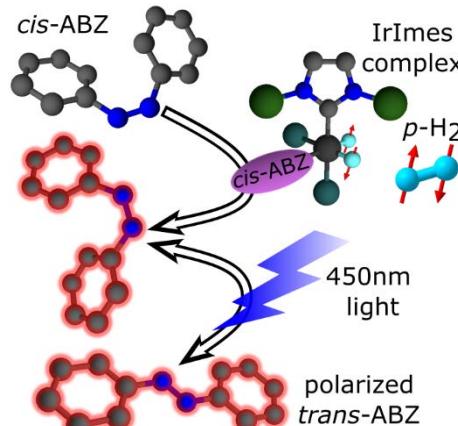


Figure 1. Schematic of the PHOTO-SABRE process, where SABRE-silent *trans*-azobenzene receives polarization from *cis*-azobenzene due to reversible photoinduced

Liquid-State Photo-CIDNP by a Synthetic Tryptophane-Linker-Flavin System

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) is a powerful nuclear magnetic resonance spectroscopy technique that generates nuclear spin hyperpolarization through optical irradiation of an appropriate donor-acceptor system^[1]. In this study, we aim to explore the photo-CIDNP phenomenon within a well-defined molecular system, focusing on the complex interactions between electronic and nuclear spins.

Our investigation utilizes specially designed synthetic dyads that feature a polyproline type II (PPII) helical structure. PPII helices are common in nature, forming the main component of collagen—the most abundant protein in humans—and are found in at least one turn in most globular proteins (Figure 1). The PPII helices serve as rigid structural motifs, acting as molecular rulers or scaffolds, providing precise control over distances between functional groups.

Building on the successful demonstration of the photo-CIDNP effect in flavoproteins^[2], we hypothesize that these synthetic dyads, incorporating a flavin group as the acceptor, will exhibit similar effects. The dyads are ideal models for this study due to their ease of manipulation and the precise control they offer over spatial arrangement and donor-acceptor distances.

The synthetic dyads we are investigating feature donor-acceptor distances ranging from 3 to 18 Å, with tryptophan or tyrosine as the donors and a flavin group as the acceptor. We are also examining the influence of different spatial orientations on the photo-CIDNP effect. The initial series of these dyads has been successfully synthesized and is currently undergoing both theoretical and experimental evaluation.

Preliminary results indicate that we have observed the photo-CIDNP effect in the liquid state, with the magnitude of the effect dependent on the distance between the flavin and tryptophan units. This finding suggests a significant distance-dependent behavior, offering insights into the spatial dynamics of the photo-CIDNP effect.

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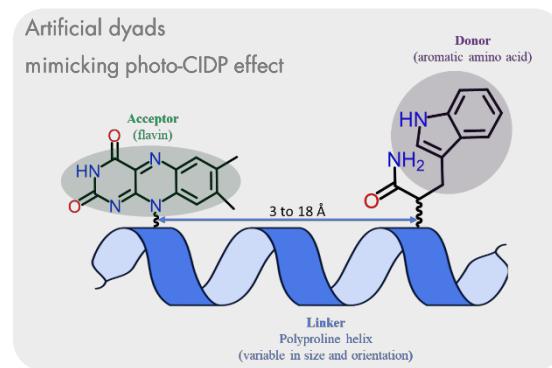


Figure 1. Synthetic dyads with varying donor-acceptor distance & spatial orientation.

C1-03

EPR and theoretical investigation of metal-free phosphorescent emitters for organic light-emitting devices

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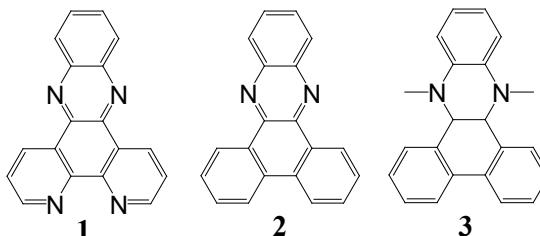
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Conjugated organic molecules have been extensively investigated for organic thin-film devices such as organic light emitting diodes. Utilization of triplet states is a key for developing organic light-emitting diodes with high efficiency. However, the preparation of metal-free room-temperature phosphorescent emitters have a high hurdle due to very weak spin-orbit coupling in pure organic molecules. Recently, we have shown that thietyl-substituted phenazines exhibit both electro-phosphorescence and electro-fluorescence at room temperature without any heavy metals [1,2]. It was found that the phosphorescence efficiency can be tuned by the orientation of fused thiophenes.

In this work, by substituting the fused thiophenes with pyridine or benzene, we examined whether the fused thiophenes are required to obtain the room-temperature phosphorescence. We found that both the pyridine- and benzene-fused phenazines (**1** and **2**) exhibit room-temperature phosphorescence without any thiophenes. On the other hand, the removal of the π -bonds at the nitrogen atoms of phenazine (**3**) led to the disappearance of phosphorescence. As shown in Figure, excited triplet states could be generated and monitored by time-resolved (tr) EPR for **1** and **2**, whereas the non-phosphorescent **3** did not show any EPR signal. It was revealed that the phenazine unit is an important role to obtain phosphorescence for the series of the π -conjugated molecules.



Scheme pyridine- and benzene-fused phenazines and related molecule.

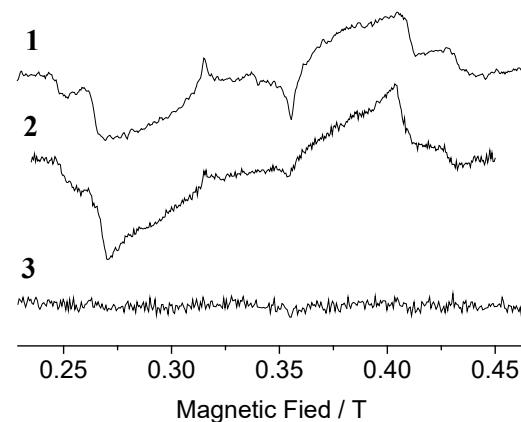


Figure. Tr-EPR of 1-3 at 40 K.

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Fast passage effect in cw-ODMR of an ensemble of NV⁻-centers

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Optically detected magnetic resonance (ODMR) is a double resonance technique that combines optical measurements with electron paramagnetic resonance (EPR) spectroscopy. In ODMR measurements, pulsed techniques are frequently used to improve the sensitivity of EPR. Applying shaped pulses controlled by the chirp and passage effect has become a major topic in manipulating spins of the optically excited states [1]. On the other hand, a continuous wave (cw) ODMR under a magnetic field has also been employed to obtain more accurate information on the zero-field splitting parameters [2]. In cw-ODMR spectroscopy, however, the passage effect has not been investigated so far.

Here, we examine the impact of the fast passage effects on field-swept cw-ODMR by using an ensemble of negatively charged nitrogen-vacancy (NV⁻) centers as a model system. Excitation in the fast passage regions can be achieved by applying a rapid-scan (RS) of the magnetic field under irradiation of cw-microwave of standard power. Figure 1 shows a concept of our study; a passage region diagram redrawn for our specified case (a) [3], and numerically calculated magnetizations in the two regions (b, c). We present experimental results and explain them by numerical analysis of time-dependent Bloch equations. Then we show that a fast passage control of a macroscopic longitudinal magnetization is crucial to efficient ODMR detection.

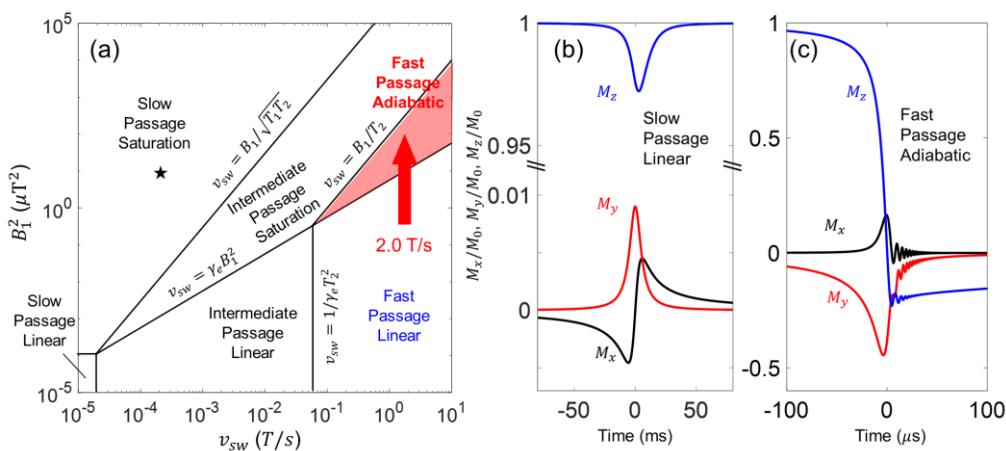


Figure 1 (a) Passage regions of magnetic resonance for v_{sw} and B_1^2 axes in logarithmic scale depicted with specific parameters, referring those of the used NV⁻ center ensemble at 100 K. Marks of ★ and a red vertical arrow indicate the examined conditions. Numerically calculated magnetizations M_x , M_y , and M_z as a function of time in (b) SPL and (c) FPA regions.

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Development and application of highly reduction resistant DNP-NMR polarizing agents

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Solid-state NMR is a powerful method for the measurement of the structural distribution of insoluble materials such as membrane proteins and amyloid fibrils. In conventional NMR measurements, it is well known that the signal sensitivity due to thermal polarization is very small. Dynamic nuclear polarization (DNP) NMR is a method to enhance the NMR signal intensity by transferring the polarization from the electron spin to the nuclear spin. The organic radicals such as nitroxide radical are widely used in DNP polarizing agents. However, these unpaired electrons are highly chemically reactive. Many DNP polarizing agents are rapidly degraded due to the strongly reducing environment such as *in-cell* condition.^[1] Novel DNP polarizing agents with high reduction resistance are required.

Nanometer scale diamond particles have a lot of unpaired electrons derived from surface dangling bond. Some DNP-NMR measurement has been reported that enhanced ¹³C signal of natural abundance inside diamond and ¹H signal of surrounding solvent.^[2] These unpaired electrons on nanodiamond are expected to be used as DNP polarizing agent *in-cell* condition due to their high chemical/physical stability. Recently, we have reported on the application of nanodiamond-based polarizing agent for DNP-MAS-NMR on biomolecules such as nanodiamond-conjugated model protein system and amyloid fibril system.^[3]

Paramagnetic metal complexes have been widely used as *in vivo* MRI contrast agents due to their resistance to reducing conditions. Recently, it has been reported that gadolinium complexes can be used as DNP polarizing agents in reducing environments.^[4] Paramagnetic metal complexes have large *g* tensor and fine structure tensor, so single-frequency microwave source is expected to be inefficient due to the difficulty excitation the optimum DNP resonance conditions. We are currently investigating the use of metal complexes as DNP polarizing agent with a variable frequency microwave source. These details will be presented.

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C1-06

Magnetic Field Effects in Avian Cryptochrome Proteins

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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. Magnetic field effects on transient absorption spectra and kinetics are reported for a variety of avian wild-type proteins and modified proteins with site specific single and double mutations. The chain of four tryptophan residues contains specific sites where spatially separated, spin-correlated radical pairs are transiently formed. In these sites an optimized geometry and orientational configuration appears to be present that enables the radicals to display strong magnetic field effects.

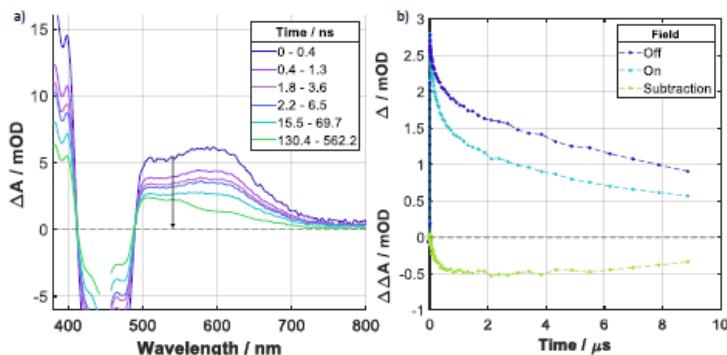


Figure 1. (a) Model transient absorption time evolution spectra for a modified avian cryptochrome. (b) Model kinetic plot of ΔA and $\Delta\Delta A$ for a modified avian cryptochrome GgCry4 W369F-Y319F at 25mT magnetic field strength.

This poster describes how specific mutations can change the magnetic sensitivity of the proteins and elucidate the different radical pair reaction pathways. The site-specific modification of the proteins reveals significant enhancements of the magneto-sensitivity that can show magnetic field effects at field strengths close to that experienced by migrating birds.

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Photo-CIDNP molecular probes for the detection of enzymes

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Abstract

Photochemically induced dynamic nuclear polarization (Photo-CIDNP) is a non-invasive hyperpolarization technique in which nuclear spin polarization is enhanced by light irradiation. The mechanism of photo-CIDNP is based on the nuclear spin selective recombination of photo-generated radical pair. Several biologically important molecules can be hyperpolarized and have been used for structural analysis of biomolecules.^[1] And in-situ photo-CIDNP has been demonstrated in MRI systems for visualizing small biomolecules and antiviral drugs.^[2,3]

Here we propose the molecular design of the "CIDNP probe" as a new generation of molecular sensors. This is the simple phenol derivative, but the hydroxy group is protected. Importantly, the oxidation potential of phenols is dramatically reduced in aqueous solution because the solvent becomes a proton accepter and proton coupled electron transfer (PCET) occurs. In other words, photo-induced radical formation and subsequent photo-CIDNP can be activated by deprotection of hydroxy groups, which is correspond to turn-on type molecular probes. These molecules can be used to detect enzymes by designing protective groups that are readily deprotected by the enzymatic reactions.

Several CIDNP probes were synthesized, and enzymatic reaction monitoring was demonstrated. CIDNP experiments were performed with benchtop NMR. The hydroxy protections were successfully inhibited the formation of radical pairs, while enzymatic deprotection enabled photo-CIDNP. The progress of the reaction could be tracked as NMR signal intensity. This strategy has been demonstrated to be applicable to a range of enzyme reactions. This is an important first step toward new applications of photo-CIDNP for medical diagnosis.

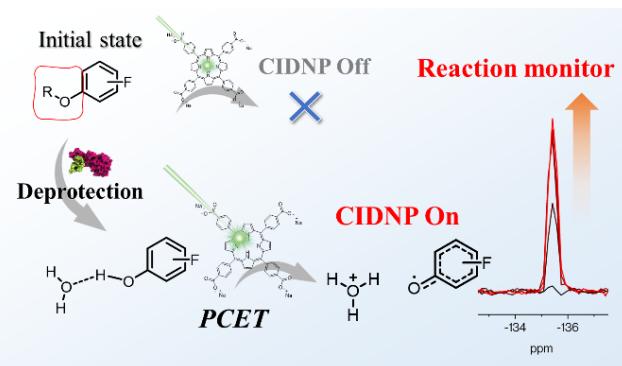


Figure 1. Concepts of photo-CIDNP probes

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C1-08

Spin chemistry in biological systems - Pushing the limits of system size using *MolSpin*

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Several studies on spin-correlated radical pairs (SCRP) in biological systems have been reported [1,2,3]. These SCRP interact with external magnetic fields (MF), altering spin-selective reaction pathways known as the radical pair mechanism (RPM) [2]. The interaction with very weak external MF, such as the geomagnetic field discussed in the topic of magnetoreception, becomes increasingly relevant [2]. However, the possible working of the RPM within biological systems, such as proteins under the influence of weak MFs, remains unclear. Additionally, the chaotic environment makes it challenging to theoretically describe spin dynamics and understand the possible effects of magnetic fields through the RPM. Two significant problems arise from this - the exponentially increasing size of the required Hilbert space due to many spin-spin interactions and the absence of accurate descriptions of stochastic fluctuations within a protein that modulate the spin-spin interactions. The commonly adopted approach for spin dynamics simulations by solving the Liouville-Von Neumann equation is unsuitable for such a multiscale problem due to the abovementioned problems.

In this work, we present an efficient approach to truncate the Hilbert size problem using Monte Carlo-trace sampling [4] and furthermore decrease the required propagation of the spin system while directly incorporating time-dependent spin-spin interactions extracted from molecular dynamics simulations and quantum chemistry calculations. The algorithm is embedded in our open-source software *MolSpin* [5,6] and can be sufficiently used for arbitrary spin systems in multiscale problems by creating a link between spin dynamics and molecular dynamics simulations.

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C1-09

Site Directed Electron Spin Polarization in Porphyrin Consisting Zr(IV) based Porous Metal-Organic Framework

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The generation of electron spin polarization is a very important procedure in the domains of quantum information science and dynamic nuclear polarization. Porphyrin-based dye molecules are frequently used in the domains of sensing and dynamic nuclear polarization. This study demonstrates the efficacy of immobilizing zinc-based porphyrin molecules as a component linker inside a stable porous Zr (IV) based framework. Porphyrin triplets on the solid surface may create spin polarization to adjacent incoming radicals immobilized through solution impregnation. The polarization generation takes place after the photoexcited species are quenched by stable radicals immobilized on the Zn(II) center, which has been validated by a series of experiments. The work demonstrates that highly compacted chromophore-porous materials has the capacity to emerge as serious contenders for future quantum applications.

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Measuring the Noise Performance of Pulsed Maser Amplifiers with a View to Practical Applications

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Amplifiers of feint microwave signals based on emissively spin-polarized materials, *i.e.* masers (microwave amplification by stimulated emission of radiation), offer two distinct advantages over conventional electronic amplifiers: (i) lower noise and thus greater sensitivity, and (ii) lower intermodulation distortion^[1] and thus greater fidelity and immunity from interference and/or deliberate jamming. On the other hand, maser amplifiers exhibit some notable disadvantages: (i) in terms of both gain and noise, they often perform far better in pulsed mode than continuously, and (ii) to operate well, or even at all, they can require the use of cryogenic refrigerators, vacuum pumps, (electro-)magnets, and/or powerful sources of light, which are bulky, fragile, power-hungry and expensive.

Over recent years, some significant improvements have been made to optically-pumped solid-state masers based on the triplet mechanism of spin polarization^[2] in molecular crystals. These include: the demonstration of quasi-continuous operation^[3] and the shrinking of the maser's footprint down to dimensions compatible with mobile applications^[4]. Towards more accurately quantifying their performance, we here study one such maser using pentacene-doped *para*-terphenyl (pc:ptp) as its gain medium, configured as a reflection-type regenerative amplifier operating at room temperature. We analyse the temporal response of its gain, bandwidth and noise temperature as well as its saturation power and dynamic range, finding that it compares favourably with the best cryogenic low-noise amplifiers (LNAs) that are commercially available. Additionally, we demonstrate both amplification and oscillation at room temperature in a pc:ptp-based maser using a single, commercially available LED as its source of pump light. Combined, our results demonstrate the promise of room-temperature maser technology as a practical means of high-fidelity ("Hi-Fi") amplification at RF/microwave frequencies in applications spanning radar, high-reliability telecommunications, and (pulsed) magnetic resonance spectroscopy/imaging.

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Spin communication in light-induced multi-spin systems

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The identification of new materials for molecular spintronics requires a deep understanding of the interactions between different spin centres.^[1] Exploiting the structural modularity of organic molecules, we investigate molecular systems in which a chromophore is covalently linked to a stable radical. In these dyads, we study the interaction between the triplet state of the chromophore, which is formed by enhanced intersystem crossing (EISC) following light-excitation, and the stable radical. Depending on the magnitude of the exchange interaction between the triplet and radical spin centres, a photogenerated quartet state may be formed. Optical spectroscopic techniques, such as femtosecond UV-vis transient absorption, and various transient EPR techniques, have been used to study the interaction between the chromophore triplet state and radical building blocks in various molecular systems.^[2] Studies on various perylene diimide (PDI)-based chromophore-radical dyads have shown that the spectral overlap of the PDI emission and the radical absorption is an important factor in optimising the triplet yield. However, in a study on BODIPY–nitroxide dyads, we also observed, that a high triplet yield does not necessarily result in a strong light-induced quartet EPR signal. In a study focusing on a PDI–TEMPO dyad a strong light-induced EPR signal was observed which can be assigned to a quartet state. When embedding an PDI–TEMPO in a polymer host matrix, we were able to demonstrate the feasibility of a coherent manipulation of the spin system at room temperature. The combined observations finally lead us to propose design guidelines for molecular systems comprising chromophores in which higher excited states can be efficiently sensitised in proximity of an unpaired electron spin.

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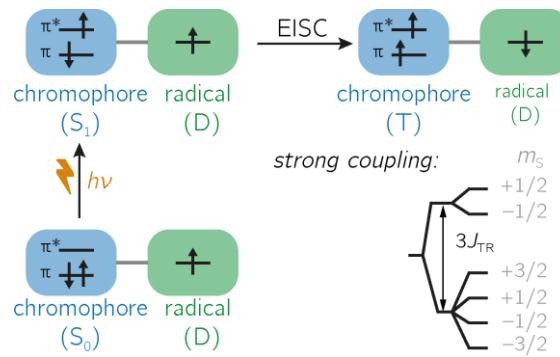


Figure 1. Following light-excitation the triplet state of the chromophore is formed by enhanced intersystem crossing (EISC). If the magnitude of the exchange interaction between the triplet spin state and the stable radical ($|J_{TR}|$) is large enough, a quartet state is formed.

Single-molecule magnetoluminescence from a stable luminescent diradical

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Luminescent radicals are an emerging class of materials that exhibit unique photophysical properties not found in closed-shell molecules due to their open-shell electronic structure. Particularly promising are photofunctions in which the spin and luminescence of radicals are correlated; for example, when a magnetic field can affect luminescence (i.e., magnetoluminescence, MagLum).^[1] However, previous observations of MagLum in radicals have been limited to systems in which radicals are randomly doped in host crystals^[1a] or polymerized through metal complexation.^[1b]

Herein, we report the synthesis, characterization, and photophysical properties of a molecule containing two spatially proximate luminescent radicals (diradical **1**, Fig. 1a).^[2] Diradical **1** dispersed in a poly(methyl methacrylate) (PMMA) matrix (0.1 wt%) showed clear changes in its emission characteristics in response to a magnetic field at 4.2 K (Fig. 1b). This is the first observation of MagLum as a single-molecule property in radical compounds rather than characteristics from aggregated or assembled radicals. Steady-state and time-resolved luminescence measurements at different temperatures and magnetic fields combined with quantum mechanical simulations indicated that the MagLum of **1** arises from a shifting equilibrium among the singlet and triplet ground states and the spin-dependent emission dynamics in the excited states. This study facilitates a detailed elucidation of the requirements for and mechanisms of MagLum in radicals, and can aid the rational design of MagLum-active radicals based on synthetic chemistry.

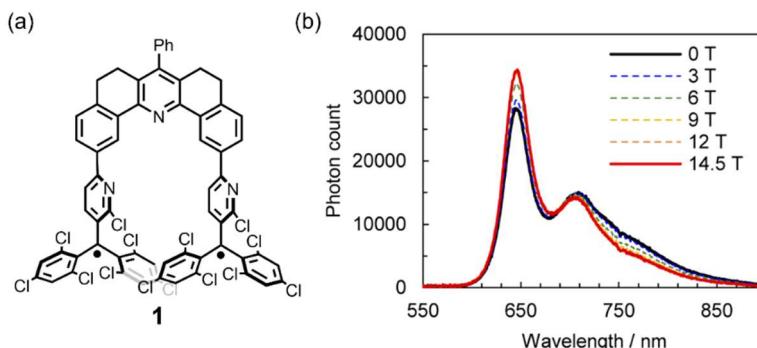


Figure 1. (a) Chemical structure of diradical **1**. (b) Photoluminescence spectra of **1** (0.1 wt%) in PMMA at 4.2 K under various magnetic fields.

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Direct observation of long-lived radical pair between flavin and guanine in DNA oligomers

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Among the four common bases in DNA, guanine (G) is the most readily oxidizable base, and the G cation radical is the putative initial intermediate in the oxidative cleavage of DNA. This oxidative DNA damage has been reported to be also caused by UV-A and visible light through dyes such as a flavin, which acts as a charge injection chromophore.^[1] On the other hand, it has been suggested that blue-light photoreceptor proteins in the photolyase/cryptochrome family including a flavin cofactor have a strong possibility of acting as highly sensitive magnetic compasses in nature.^{[2]-[6]} The mechanism is presumed to be that when flavin adenine dinucleotide (FAD) in photolyase/cryptochrome is irradiated with blue light, electron transfer occurs from tryptophan (Trp) with charge separation (CS) to generate a radical pair (RP) between flavin and Trp. Here, we will present the first observation of a long-lived radical pair between flavin and G base in DNA oligomers, and discuss the reaction mechanism.

This work was supported by the Watanabe Foundation, the Sumitomo Foundation, JSPS KAKENHI Grant Numbers JP16K13980, 22K05053 and 22H02053.

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MOF catalyzed ortho–para hydrogen conversion

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Abstract

The use of liquid hydrogen as a fuel is a promising alternative to fossil fuels. Molecular hydrogen can exist in the form of two nuclear spin isomers - ortho-hydrogen and para-hydrogen; however, safe storage and transportation can be realized only for para-hydrogen. Therefore, liquefied hydrogen is subjected to ortho-para conversion using paramagnetic catalysts. In industry, iron oxide-based catalysts (e.g. Ionex®) are commonly used for ortho-para conversion of hydrogen. However, these materials have rather low porosity and availability of metal ions for hydrogen. On the other hand, the porosity and availability of paramagnetic metal ions for hydrogen is much higher in metal-organic framework (MOFs), which have attracted considerable attention of the scientific community in recent years.

In this work, we studied the efficiency of a number of MOFs catalyst in the process of ortho-para conversion of hydrogen. As part of a systematic study of MOFs as catalysts for this process, it was found that the specific rate constant of ortho-para conversion on the MOF surface is more than 100 times higher than that of commercially used catalysts[1].

This work was supported by the Russian Science Foundation (No. 22-73-10239).

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A Novel Simulation Framework for Spin-Correlated Radical Pairs

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Photogenerated radical pairs (RPs) play an important role in a variety of biological processes, typically as short-lived intermediates in cascades of chemical transformations. Recently, they have gained interest as two-qubit models for quantum information processing in chemical architectures and as ideal systems to explore novel aspects of chirality-induced spin selectivity (CISS).^[1,2] However, the theoretical assessment of optimal protocols for quantum sensing with RPs is hampered by the complex interplay of their coherent spin and incoherent electron transfer dynamics. This is especially true for all-optical detection of RP spin dynamics *via* optically detected magnetic resonance (ODMR), where coherent spin dynamics are monitored *via* fluorescence. Existing simulation frameworks for conventional NMR and EPR^[3,4] are not particularly suited to model these effects, which is further challenged by the computational demand of propagating the RP's high-dimensional Liouvillian.

Here, we introduce a newly developed Python-based software package designed specifically for the simulation of ODMR experiments. The simulation package enables simple construction of the Liouville space, with ready-to-use functions for straightforward generation of all suitable Hamiltonian contributions to the Liouvillian and the incoherent part in the form of classical Lindblad collapse operators. We discuss recent approaches that exploit state-of-the-art computing hardware to leverage massive parallelism.^[5] Finally, we demonstrate the software for photogenerated RPs and propose experimental schemes for all-optical assessment of the RP's initialization and evolution of triplet character. Since a non-zero triplet fraction in the initial state of the photogenerated RP has been hypothesized to arise due to CISS, the proposed experiments could provide insight into the peculiar spin dynamics of chiral environments.

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Probing charge extraction in organic solar cells using spins

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Organic Solar Cells (OSCs) are considered a promising solar technology because of their high degree of tuneability. In organic solar cells, electricity is generated by photoinduced charge separation at a donor:acceptor interface followed by extraction of the created charges. After the initial charge separation step, electron and holes have to travel to the electrodes typically through charge hopping. If opposite charges re-encounter after charge separation, they can also recombine, resulting in an energy-loss pathway.^[1] Charge transport and charge recombination determine the efficiency of charge extraction and, consequently, the overall performance of organic solar cells and both processes are governed by spin selection rules and are therefore spin-dependent.

Electrically Detected Magnetic Resonance (EDMR) spectroscopy is a very effective technique to gain a better understanding of spin-dependent charge transport and recombination. EDMR measures changes in current flowing through a fully assembled device induced by microwave pulses, which affect relative spin orientations and allow previously spin-forbidden hopping or recombination.^[2] Only spins involved in current generation are measured under operando conditions, making EDMR exceptionally suited to investigate photovoltaic devices.

This work focuses on investigating OSCs with active layers based on different organic donor and acceptor materials, including fullerene and non-fullerene acceptors, using pulse EDMR^[3] at cryogenic temperatures. EDMR-detected Rabi nutations and Hahn echo experiments provide information on the role of donor and acceptor in charge transport and recombination processes and allow identification of the dominant spin-dependent process photo-excited charges undergo in their journey from the donor:acceptor interface to the electrodes.

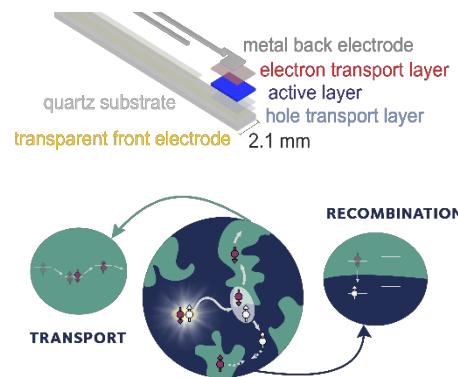


Figure 1. Schematic representations of the structure of an OSC used for EDMR measurements and of the spin-dependent charge transport and recombination processes in the active layer of an OSC.

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A2-03

Theoretical analysis of spin-orbit charge-transfer inter-system crossing (SOCT-ISC) mechanism forming long-lived triplet excited state

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Metal-free organic triplet photosensitizer is an attractive area of material science, in particular the use of a donor-acceptor linked chromophores is promising because its charge transfer state (CT) has a long lifetime and often exhibits efficient intersystem crossing due to the spin-orbit coupling induced by charge transfer (SOCT-ISC). In the previous research, it was reported that BDP-PXZ-2, a dyad of bodipy (BDP) as acceptor and phenoxazine (PXZ) as donor, exhibit a TR-EPR spectra consisting of two different transient species assigned to ³CT (PXZ→BDP) and ³BDP, while that of the methylated derivative BDP-PXZ-1 is well explained by ³BDP alone^[1]. Most of the molecular mechanism of these processes has been still uncertain. Thus, in this theoretical study, we elucidated the detail of triplet formation process of BDP-PXZ-1 and BDP-PXZ-2 and the reason why the two different transient species coexist for the BDP-PXZ-2.

The potential energy curves along with dihedral angle between BDP and PXZ moieties were evaluated using the time-dependent density functional theory (TD-DFT) and revealed that the absence of the CH₃ moiety, which is electron donor group, stabilizes ³CT state of BDP-PXZ-2 and allows the co-existence of two triplet states detected by the TR-EPR experiments. We also investigated the spin orbit coupling (SOC) between ¹CT (PXZ → BDP) and each triplet state of BDP-PXZ-2 at the orthogonal conformation, nearby the crossing point of the states, and found that the ISC is spin selective and the generated triplets should be spin polarized to the component of the BDP's long axis (x molecular axis). The calculation of zero-field splitting (ZFS) parameters on ³CT and ³BDP was performed with the CASSCF theory. These results well-reproduce the spectra of experimental TR-EPR, which strongly support the SOCT-ISC mechanism we propose.

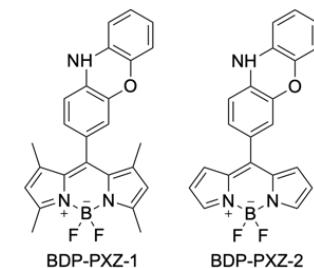


Figure 1. Structures of BDP-PXZ dyads

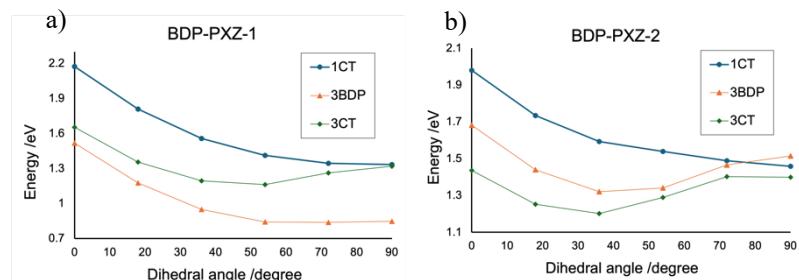


Figure 2. Calculated excited state potential energy curves at 1CT optimized structures in toluene solvent effect: a) BDP-PXZ-1, b) BDP-PXZ-2

Table 1. Theoretically calculated ZFS parameters and experimentally determined value

BDP-PXZ-2	D [mT]	E [mT]
³ BDP (calc.)	-80.06	6.12
³ BDP (exp.)	-82.1	19.1
³ CT (calc.)	-41.25	-13.22
³ CT (exp.)	-37.5	8.2

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A2-04

Materials and Methods for Chiral Induced Spin Selectivity

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As first formulated, the Chiral Induced Spin Selectivity (CISS) effect refers to the ability of chiral materials to act as spin filters for electron transport. Later observations have also shown a connection between electron spin and chirality without the need for net charge flow. The field has been increasingly explored for its potential in spintronics, spin-optoelectronics and quantum applications. Experimental observations are copious and make use of different techniques, while there still is no agreed theory on the effect. [1]

To fully unleash the potential of CISS, not only deeper understanding of the underlying theory is required, but also the development of techniques and materials that allow its exploration in a systematic way. Following previous work done in the group, materials science is used to understand the role of directionality and alignment of the chiral layer in CISS. [2] The assembly of chiral materials in thin films is not only studied, but also driven by templating methods. Deposition techniques that could easily be adopted for device fabrication are used, such as spin coating or Organic Molecular Beam Deposition (OMBD). The conductivity and spin polarisation of the films is also studied, with the goal of developing highly controllable chiral layers with tuneable properties for a wide range of applications in spintronics and spin-optoelectronics.

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Understanding Triplet Spin-Optical Properties of Chiral Bi-Carbazoles

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Carbazole moieties are electron-rich groups often employed as building block components of charge transport, host and functional materials for organic light-emitting diodes (OLEDs).^{1,2} Their application in optoelectronic devices is established, however understanding charge and exciton mechanisms arising from these systems is essential for improving their performance.^{1–3}

Bi-carbazole dimers can functionalize organic emitters with a chiral twist that enables circularly polarised luminescence (CPL).⁴ Control of CPL in OLEDs could maximize light output from displays due to anti-glare filters that function by blocking light of a certain handedness of circular polarisation.⁵ Chiral molecules, such as bi-carbazole dimers, have demonstrated CPL, with the handedness being tied to the molecular structure.^{6,7} The factors that underpin the handedness of CPL in chiral bi-carbazole molecules are tied to the molecular structure and will be relevant to the potential device performance of those molecules.

Here we investigated the spin-chiroptical properties of a series of carbazole monomers and bi-carbazole dimers. The mechanisms underlying the formation of triplet excitons were probed by transient electron paramagnetic resonance studies, and chiroptical studies revealed the fluorescence and phosphorescence emission polarisation.

We revealed that for bi-carbazoles both opposite and identical handedness of CPL in fluorescence and phosphorescence depends on the molecular structure. This experimental work was supported by theoretical studies towards establishing structure-function relationships for molecular design of spin-orbit coupling to target chiroptical behaviour.

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Excited State of Heptacene Studied by Electron Spin Resonance

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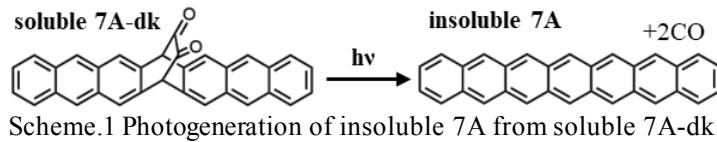
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Although n benzene-fused acene (**nA**) is the core aromatic compound in chemistry and is a prospective building block of narrow bandgap semiconductors for organic optoelectronics, there are many open questions about the excited states of **nA** with $n \geq 6$ due to the high reactivity and the insolubility of large acenes. Heptacene diketone (**7A-dk**) is a soluble photo-precursor to generate insoluble heptacene (**7A**, Scheme. 1).^[1-3] This photo-precursor is a potential molecule to solve the difficulties in spectroscopic studies on the excited state of **nA**. Therefore, we have been investigating photochemistry of **7A-dk** in various matrices such as PMMA so far.^[4] In this paper, we will show the excited triplet states of **7A** photogenerated from **7A-dk** in a glassy matrix of *o*-terphenyl at room temperature, mainly using time-resolved ESR (tr-ESR). **7A-dk**-doped *o*-terphenyl (0.5 mM) in a quartz tube sealed under 2×10^{-1} Pa was used for the experiments.

By measurements of absorption spectrum, it was revealed that not only **7A** but also byproducts with **5A** and/or **4A** units (**5A'** and **4A'**) were generated from **7A-dk** in *o*-terphenyl by irradiation of laser light (440 nm), corresponding to the $\pi^* \leftarrow n$ transition of the diketone, at room temperature for hours. Fig. 1a indicates tr-ESR spectrum observed in selective excitation of the photogenerated **7A** by irradiation at 640 nm. The zfs constants of **7A** ($|D| \sim 0.042 \text{ cm}^{-1}$, $|E| \sim 0.001 \text{ cm}^{-1}$) are slightly smaller than that of **5A**. Tr-ESR spectra of the excited triplet states for **5A'** and **4A'** were also detected by irradiation at 440 nm (Fig. 1b). The zfs constants for **5A'** and **4A'** are respectively the same as **5A**^[5] and **4A**^[6].

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Scheme 1 Photogeneration of insoluble **7A** from soluble **7A-dk**.

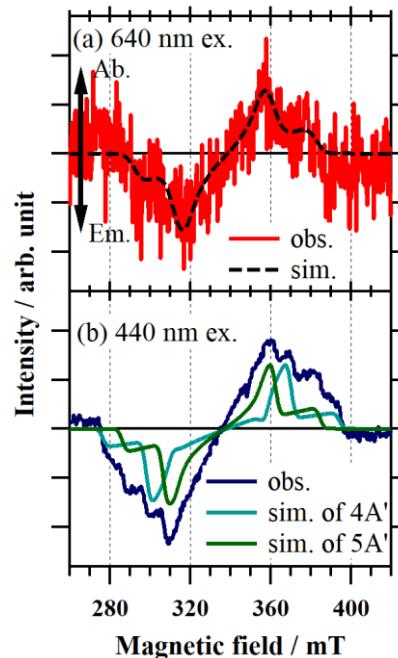


Fig. 1 Tr-ESR spectra detected at 1 μ s after the laser pulse at the wavelengths of 640 nm (a) and 440 nm (b).

Chemical quantum sensing using acene-based metal-organic frameworks

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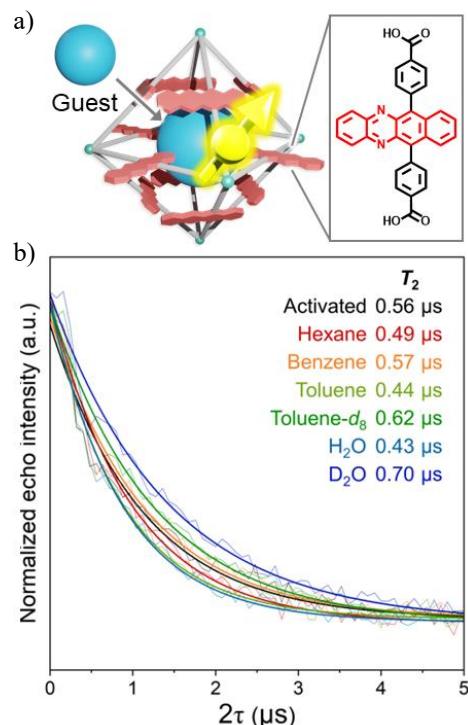
The qubit is the most basic unit in quantum information science. Among various qubits, molecular qubits using electrons are useful because the structure can be created precisely, and their properties can be controlled by chemical structure. Quantum sensing is a method of measuring quantities using qubits. It is expected to achieve higher sensitivity than conventional sensing. For such sensing applications, qubits must have a long coherence time (T_2) and response to external stimuli.

Recently, nanoporous metal-organic frameworks (MOFs) have attracted attention as a platform of quantum sensors. MOFs consist of metal ion and organic ligand, and their electrons can be used as qubits. MOFs can encapsulate guest molecules and qubits can be close enough to interact with them.

We have previously observed radicals with long T_2 in MOFs with 5,12-diazatetracene (DAT) derivative^[1,2]. T_2 of that MOF responded to paraffin, which suggests that MOF has guest responsiveness for quantum sensing. However, it was difficult to introduce various guest molecules due to limited structural stability. In this study, we synthesized a novel rigid and stable MOF with a DAT-containing ligand. This MOF enables the stable guest introduction and evaluation of the effect of guest inclusion on T_2 of DAT radicals created in the ligands. Compared to activated (no guest) MOF, water, toluene, and hexane showed a shorter T_2 . On the other hand, in the case of deuterium solvents T_2 were longer. Thus, T_2 of radicals in MOF with DAT is affected by the hyperfine interactions with guest molecules and the motion of DAT ligand in the MOF structure^[3].

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chemical quantum sensing using an acene-based MOF. b) Decay of the echo intensity of the Hahn-echo sequence for the MOF at room temperature.

A2-08

Spin coupling through bond and space in light-induced multi-spin systems

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Light-induced multi-spin systems receive increased attention recently due to their exceptional properties and their potential for applications in molecular spintronics.^[1,2] Assemblies consisting of a chromophore, a linker and a radical, are excellent model systems to investigate spin–spin interactions and high-spin states.^[3] Light excitation generates a triplet state at the chromophore moiety, which may interact with the stable organic radical.

Several studies on covalently-linked chromophore–radical pairs suggest that the exchange interaction, which is considered a through-bond interaction, governs the formation of quartet states.^[1,2]

Within this study, the magnetic properties of the covalently-bound system are compared with those of the non-covalently-bound systems, including hydrogen-bonded and bimolecular pairs as shown in Fig. 1. The transient pulse EPR data suggest that quartet states are formed even in non-covalently-bound systems, demonstrating that supramolecular chemistry could provide the missing piece of the puzzle to enable the scalability of organic spin qubits.

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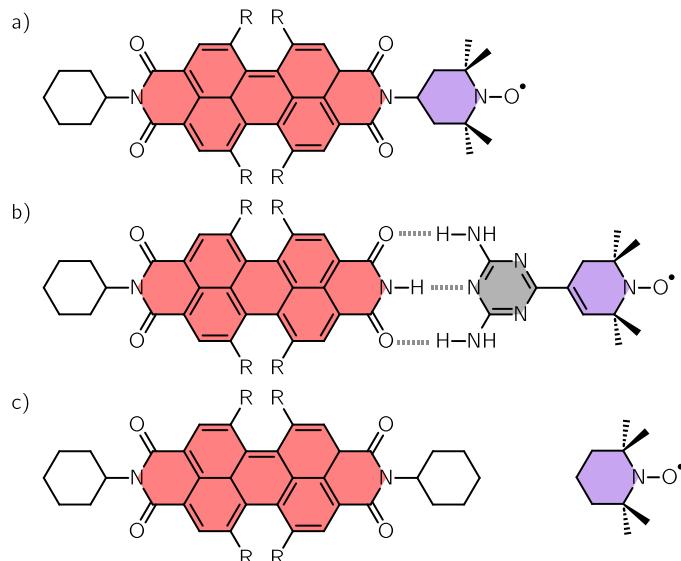


Figure 1. The investigated chromophore–radical systems.
a) Covalently bound PDI–TEMPO as known reference system,
b) supramolecular hydrogen bonding approach,
c) bimolecular approach.

Simultaneous Measurement of Magnetic Field Effects on Photocurrent and Optical Absorption Signals of PTB7:PC₇₁BM Bulk Heterojunction Film

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Elucidation of the exciton and carrier dynamics is important to improve energy conversion efficiency of organic solar cells. A high energy conversion efficiency of 9.2 % has been reported for bulk heterojunction (BHJ) thin film solar cells using a polymer PTB7 and a fullerene derivative PC₇₁BM (Figure 1).^[1] In this study, we investigate the effect of paramagnetic intermediates on charge carrier generation by measuring magnetic field effect (MFE) using the Simultaneous Optical-Electrical Detection, which allows quantitative evaluation of charge number density and mobility.

The thin film was deposited on a quartz substrate with interdigital gold electrode using the spin coating method.^[1] The film was excited at 532 nm using the nanosecond pulsed laser. The transient absorption (ΔA) at the wavelength of 990 nm (absorption wavelength of the hole in PTB7) was measured using the Xe lamp as a probe light source. The transient photocurrent (Δi) associated with the pulsed laser irradiation was measured under applied external bias voltage.

Figure 2 shows the MFEs on ΔA and Δi ($MFE_{\Delta A}$ and $MFE_{\Delta i}$) for the BHJ film. For both $MFE_{\Delta A}$ and $MFE_{\Delta i}$, positive MFEs are observed, and the half magnetic field ($B_{1/2}$) are about 80 mT. The similar $MFE_{\Delta A}$ and $MFE_{\Delta i}$ indicates that the charge number density increases with magnetic field. Since the MFE is observed at the instrument response time (~10 ns) and the MFE amplitude does not depend on the excitation intensity, it is considered that unimolecular deactivation of a short-lived (<< 10 ns) paramagnetic intermediate is prohibited by the magnetic field. The short-lived intermediate is considered to be an excited triplet state because $B_{1/2}$ is comparable to the zero-field splitting in excited triplet molecules.

It has been reported for the PTB7 film without PC₇₁BM that the similar $MFE_{\Delta A}$ is observed on the generation yield of the long-lived (~ μs) triplet state.^[2] We confirmed that this MFE is also independent of excitation intensity. We propose the d-type triplet mechanism due to a spin-polarized short-lived triplet PTB7 as the cause of the MFE. In the BHJ film, the hole and electron are generated by electron transfer from this short-lived excited triplet to PC₇₁BM, so that the same MFE is observed for those carriers.

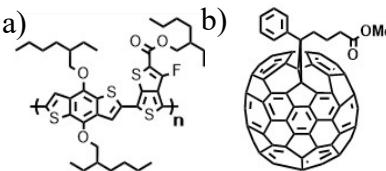
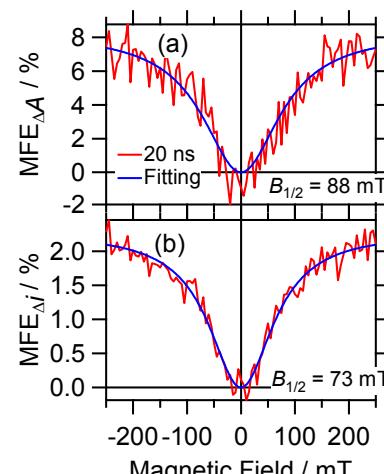


Figure 1. a) Structure of PTB7, and b) PC₇₁BM



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Generation of large and long-lived electron spin polarization of TTM radical derivatives for optically-driven DNP

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Chemically induced dynamic electron polarization (CIDEP) due to the interaction between photoexcited chromophores and radicals can achieve high electron spin polarization even in solutions at room temperature. By combining CIDEP with Overhauser DNP, it is possible to enhance NMR signals in solutions using only light irradiation, without the need for microwave irradiation.^{[1], [2]} In previous studies on optically-driven DNP, nitroxyl radicals, such as the TEMPO radical, have been predominantly used as stable radicals. However, there have been no reports on optically-driven DNP using other radical species.

In this study, we report the first example of solution-phase CIDEP and optically-driven DNP using tris(2,4,6-trichlorophenyl)methyl (TTM) radical derivative (TTMDFA, Fig.1a).^[3] Upon photo-excitation of tetraphenylporphyrin (H₂TPP, Fig.1b) chromophore, the polarization signal derived from the TTMDFA radical showed a larger ESR signal than that of the TEMPO polarization signal (Fig.1c). Furthermore, since the energy of the D₁ state of TTMDFA is lower than the T₁ state of porphyrin, efficient CIDEP is achieved through the quenching of the chromophore T₁ state via energy transfer to the radical D₁ state. Optically-driven DNP using porphyrin-TTMDFA showed a much greater difference in NMR signal intensity compared to porphyrin-TEMPO (Fig.1d). This improvement is attributed to the enhanced saturation factor by larger and longer-lived polarization of the TTM radical, revealing the promising potential of TTM radicals in optically-driven DNP.

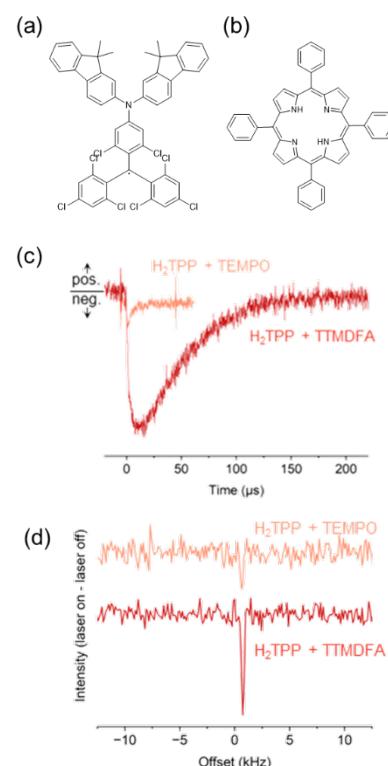


Figure 1. a) Chemical structure of TTMDFA and b) H₂TPP. c) Decays of ESR signal and d) the differential spectra of ¹H-NMR signals of toluene between with and without laser irradiation containing H₂TPP and TEMPO (light red line), and H₂TPP TTMDFA (red line).

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A2-11

Mapping the Influence of Orientation and Distance of SCRP on solid Photo-CIDNP effect in a Multi-Tyrosine Flavoprotein System

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Photo-Chemically Induced Dynamic Nuclear Polarization (Photo-CIDNP) is one of the hyperpolarization methods that enhances NMR signals by generating non-Boltzmann nuclear spin magnetization through spin-correlated radical pairs (SCRP) created by photoexcitation ^[1]. Flavoproteins have served as valuable models in previous studies exploring the mechanisms underlying the Photo-CIDNP effect ^{[2][3][4][5]}.

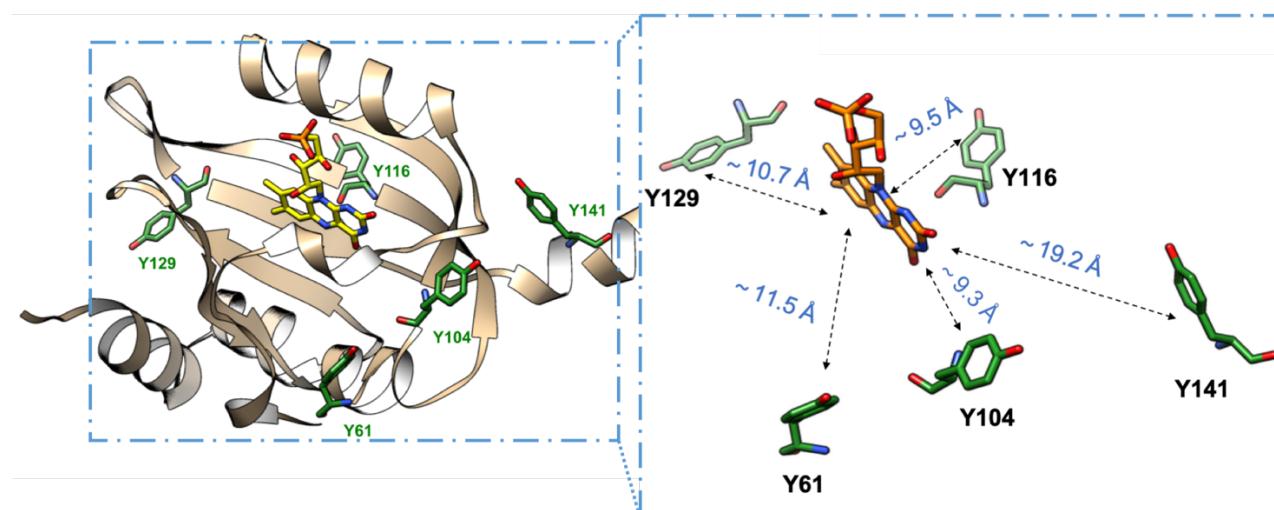


Figure 1. Structural model of the LOV domain Mr4511 with highlighting the position of tyrosine.

The light-oxygen-voltage (LOV) domain 4511 from *Methylobacterium radiotolerans* (Mr4511) is a flavoprotein with multi-tyrosine as electron donners and FMN as electron receptor, which shows significant solid-state Photo-CIDNP signal enhancement in ¹³C natural abundance. By applying site-directed mutagenesis to the system, with the helping of UCSF Chimera to model the spatial configuration of tyrosine residues and the FMN, different hyperpolarization enhancements with varying orientations and distances relative to SCRP were mapped, showing orientations and distances between electron donner and electron receptor playing crucial roles in the efficiency of the solid-state Photo-CIDNP effect.

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Theoretical study on spin polarization via charge-transfer states in complex-radical connected systems

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Introduction

Chromophore-radical connected systems have recently attracted much attention for their applications in spin chemistry, including molecular magnetism and quantum information science. The photo-induced electron spin polarization originating from their doublet/quartet spin states is interesting, yet specific mechanisms are still largely unexplored. As a category of such molecules, the Pt and Pd metal complex-radical connected systems (**Fig. 1(a)**) have been reported by Kirk *et al.* in recent years^[1,2,3]. These molecules exhibit interesting photo-induced spin polarization dependent on the central metal atoms and linker substituents. To investigate the relationship between molecular structures and the spin polarization effect, we performed excited state calculations using multi-reference electron correlation theory.

Method and Results

For excited state calculations, we adopted the CASSCF/CASPT2 method to account for advanced electron correlation effects. The active space included the π -orbitals of the chromophore, linker and radical.

Calculated excited state energies are depicted in **Fig. 1(b)**. Vertical excitation energies for all molecules closely matched the experimental data from UV-Vis absorption spectra. We also revealed the energy ordering of multiple excited states. Furthermore, we conducted calculations regarding the magnitude of spin-orbit coupling between different excited states. The spin-orbit coupling values in Pt complexes were found to be greater than those of Pd complexes.

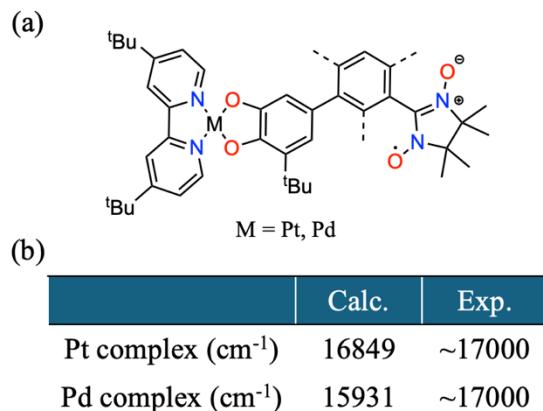


Figure 1. (a) Pt and Pd complex-nitronyl nitroxide radical connected systems reported by Kirk *et al.* (b) Calculated and experimental energies of the vertical excitation state.

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Electronic structure of 5-deazaflavin radicals: a photo-CIDNP study

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5-Deazaflavins are important analogs of biologically relevant flavins, such as riboflavin or flavin mononucleotide (FMN). They are often employed in cofactor replacement experiments to understand and modify reaction pathways of flavoproteins [1]. It was assumed that the stability of the 5-deazaflavin radical is significantly lower compared to the flavin semiquinone as one-electron-transfer reactions are frequently impeded in flavoproteins with 5-deazaflavin as a cofactor [1-2]. This long-standing paradigm of 5-deazaflavin being unable to transfer single electrons needs to be reevaluated with our observation of a one-electron reduced species using photo-chemically induced dynamic nuclear polarization (photo-CIDNP) NMR spectroscopy [3].

Photo-CIDNP is a versatile tool to investigate mechanisms in the context of light-induced radical pair reactions. 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 nuclear spin-sorting. Analysis of the experimental data gives access to the hyperfine pattern of the SCRP and provides important mechanistic details of the investigated radical pair reactions [4].

Using photo-CIDNP spectroscopy, we were able to detect and characterize the 5-deazaFMN radical under physiological conditions [3]. Based on these findings, we conducted a thorough investigation of the electronic structure of the 5-deazaFMN radical using ¹H and ¹³C photo-CIDNP NMR spectroscopy over a wide pH range. By studying demethylated 5-deazariboflavin analogs, the influence of substituents at position 7 and 8 of the 5-deazaisoalloxazine moiety is assessed [5]. These findings may ultimately allow a deeper understanding of the different electrochemical and photochemical reactivities of flavins and 5-deazaflavins.

This research was funded by the Deutsche Forschungsgesellschaft (DFG), grant number 459493567 (WE 2376/12-1 and FI 824/13-1).

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Elucidation of Initial Charge Separation Structure in Y-series Non-Fullerene Acceptor-Based Organic Thin Film Solar Cell by Time-Resolved EPR and Pulse EPR

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Organic thin-film solar cells have extensively been studied as lightweight and low-cost solar cells to improve the power conversion efficiency (PCE). In this study, we employed low-temperature time-resolved EPR (electron paramagnetic resonance) spectroscopy and pulse EPR spectroscopy to measure and analyze the photoactive layer of organic thin-film solar cells composed of DP-2 of the Y-series NFA and PBDB-T of the donor. We determined the radical structures at the initial charge separation stage. Figure 1 shows OOPSEEM trace of the PBDB-T/DP-2 blend film at 80 K with DAF = 500 ns (left black) and the radical distance distribution density for the initial charge separation state (right) obtained from simulation of the OOPSEEM trace (left red) [1]. From the OOPSEEM results, a peak of 3.0 nm and a peak of 3.4 nm were expressed. The value of 3.0 nm obtained by TREPR is consistent with this peak. The reason for the absence of the distribution with a broad range with a peak at 3.4 nm in the TREPR is that the exchange interaction (J) is very small at larger distance, hiding to exhibit the weak spin polarization intensity in the TREPR. Thus, radical pairs with orientations for which J is comparable to the hyperfine coupling are only observed in the TREPR, while the OOPSEEM shows various distance distributions of radical pairs to cause the lower frequency echo modulations by the dipolar coupling. The spin-lattice relaxation time (T_1) is relatively fast even at low temperatures, which may represent an entropy effect that promotes charge separation.

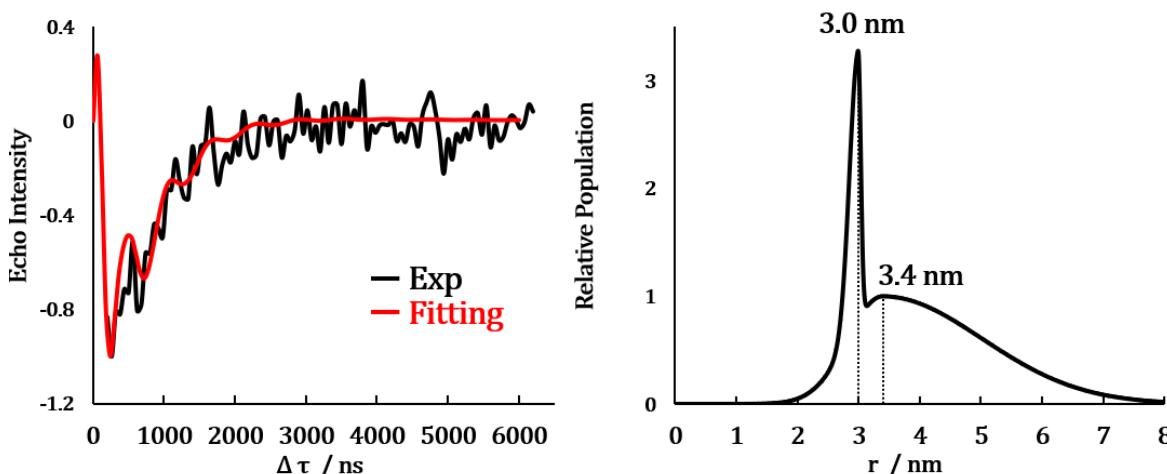


Fig.1 OOPSEEM trace of the PBDB-T/DP-2 blend film at 80 K (left black) and spectrum simulation (left red) with DAF = 500 ns. The radical distance distribution density for the initial charge separation state (right) obtained from simulation of the OOPSEEM trace.

Light-Harvesting Spin Polarization of Organic Radical in a Metal-Organic Framework

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Electron spin polarization (ESP) through photoexcitation of chromophore-radial (C-R) systems is a crucial technique for the spin-based applications such as quantum information science (QIS)^[1] and dynamic nuclear polarization (DNP)^[2]. Synthetic chemistry enables scaling up of a single electron spin to functionalized multi-spin arrays, thereby broadening the scope of these applications. However, achieving efficient light-driven ESP in mesoscopic structures has remained challenging, primarily because most of C-R systems are dispersed in a 1:1 ratio of C-R within a glass matrix to ensure uniform ESP upon photoexcitation of the chromophore.

In this study, we propose a novel approach called light-harvesting spin polarization, which utilizes a metal-organic framework (MOF) as a light-harvesting antenna. Specifically, we employed a porphyrin-based Zr-MOF, MOF-525, where CTEMPO radical was introduced via postsynthetic modifications (Fig. 1a and 1b).

Fig. 1c shows the time-resolved EPR (TREPR) spectra of MOF-525 with varying doping ratios of CTEMPO after photoexcitation. All samples showed ESP of CTEMPO as the central absorptive signal, attributed to singlet exciton quenching of porphyrin by CTEMPO. This ESP was observed even with a 1% doping ratio of CTEMPO, facilitated by singlet exciton migration throughout MOF-525. The Stern-Volmer plot of the fluorescence quenching indicated that singlet excitons migrated approximately 35 porphyrin units.

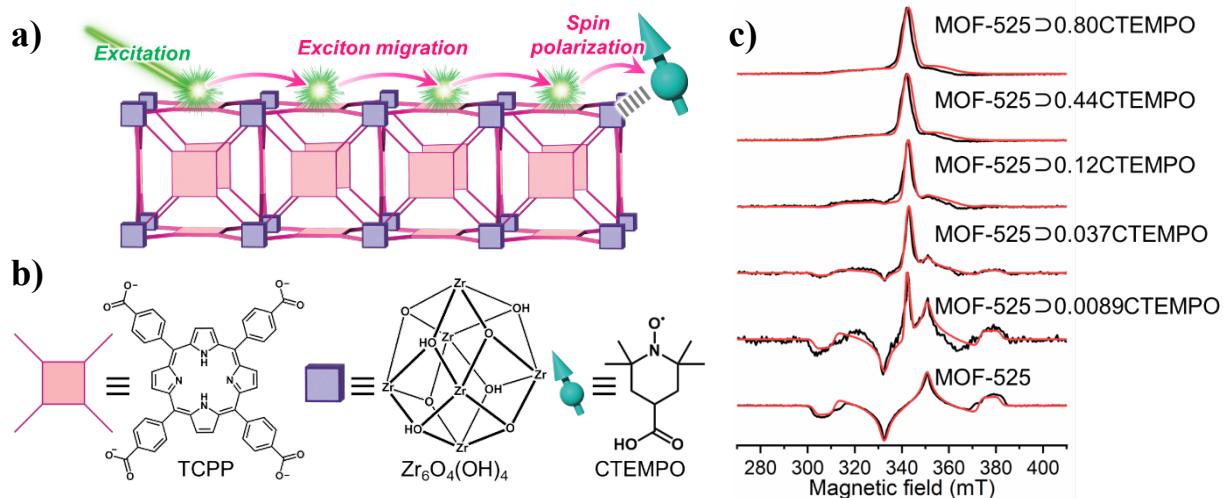


Figure 1. a) Schematic illustration of the light-harvesting spin polarization in MOF-525 \supset CTEMPO.
b) Molecular structures. c) TREPR spectra of MOF-525 varying doping ratios of CTEMPO.

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Radical pair library for photo-CIDNP

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NMR spectroscopy and imaging provide us useful information across wide range of scientific fields such as physics and biology. However, low sensitivity due to low polarization at thermal equilibrium poses substantial barrier to the applications of this technology. Photochemically induced dynamic nuclear polarization (photo-CIDNP) is a potentially convenient solution to realize highly sensitive NMR. The theory of photo-CIDNP is postulated by Kaptain^[1] and Closs^[2] independently in 1969, which enables hyperpolarization of nuclear spin through a radical pair mechanism triggered by light irradiation to the combination of a dye (D) and a quencher (Q). In this mechanism, nuclear polarization is enhanced via spin-selective intersystem crossing (ISC) of the photochemically generated radical pair (Fig. 1a). Despite the large body of photo-CIDNP, realizing high polarization is still challenging due to the involvement of multiple parameters. Therefore, proper combinations of D and Q have been sought.

In this study, we explored photo-CIDNP enhancement in numerous combinations of dyes including Rose Bengal (RB) and tetraarylporphyrins (TAPs) (Fig. 1b), paired with over 100 different quenchers. For future medical application, we performed NMR measurements using the same magnitude of the magnetic field (1.5 T) as that used in MRI. Some RB-Q pairs exhibit photo-CIDNP, however, continuous photoirradiation makes it decomposed due to the low photostability of RB. In contrast, TAP-Q pairs show photo-CIDNP as well, without any noticeable degradation under photoirradiation for 1 min. This robustness insures the persistent photo-CIDNP response. In addition, the relationship between the photo-CIDNP enhancement and several parameters, i.e. difference of g-value between radicals (Δg), HFCC of corresponding radicals and free-energy of electron transfer (ΔG_{ET}), was investigated in detail.

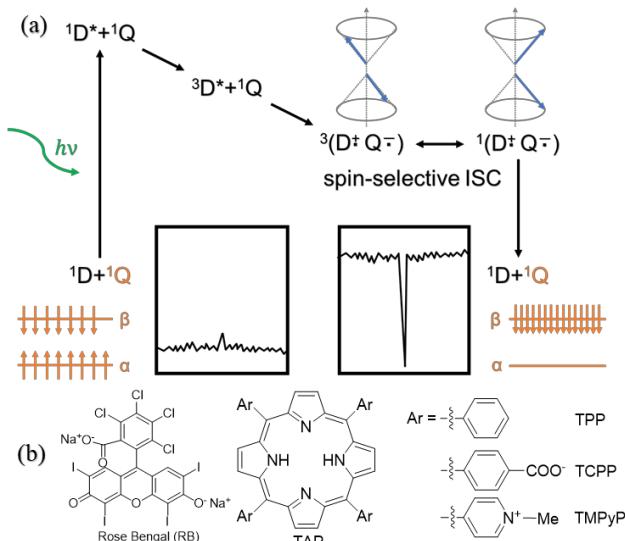


Figure 1. (a) Schematic representation of photo-CIDNP.
(b) Chemical structures of RB and TAPs.

References:

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A Macrocyclic Parallel Dimer Showing Quantum Coherence of Quintet Multiexcitons at Room Temperature

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Quantum information science (QIS), an application of quantum mechanics, is revolutionizing a wide range of fields from computing to communications and sensing. As the fundamental elements of QIS, molecular-based quantum bits (qubits) have the advantage that their structure is uniform at the atomic level and their structure and properties can be precisely controlled by chemical modification. It is essential for any quantum applications to prepare the initial pure quantum state in the qubit and to have a sufficiently long quantum coherence time. Singlet fission (SF) can generate a quintet triplet-pair state with four entangled electron. Recent theoretical studies have shown that when the orientations of the chromophores are parallel, it is possible to selectively populate certain sub-levels of the quintet. In addition, strong exchange couplings (J) can make quintet spin coherence long-lived.

Here we report the synthesis of a macrocyclic parallel dimer (**MPD**) and the observation of long-lived quintet quantum coherence even at room temperature. Continuous-wave transient EPR measurements and analysis have revealed spin-selective quintet population with large J . Subsequent pulsed EPR measurements have revealed the spin coherence time (T_2) of quintet spin was 648 ns at room temperature, which is nearly 5 times longer than the previous MOF system. This is because the structural fluctuations of the pentacene units in the **MPD-1** dimer were kept small. Unlike previous MOF systems, the homogeneously dispersed dimers have the advantage that the component with the long coherence time is major. Further fine tuning of linker and chromophore structures would provide a wide range of attractive MPDs from a viewpoint of flexibility, distance, orientation, and stability.

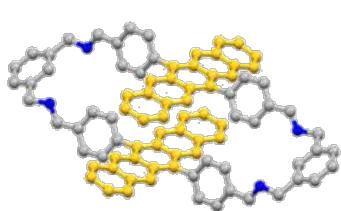


Figure 1. The single crystal structure of **MPD-1**.

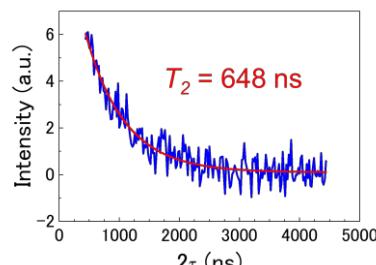


Figure 2. Spin coherence time of **MPD-1** in polystyrene at room temperature.

B2-01

Magnetosensitivity in Lipid Peroxidation: Defying Diffusion and Strong Inter-radical Coupling

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Magnetic fields have been shown to alter the rate of lipid peroxidation *in vivo*, for which a radical pair model (RPM) is thought to be responsible [1]. Prior theoretical investigations have considered static radical pairs, or radical triads [2]. In doing so, these have neglected the impact on the dynamics from diffusion of the radicals. This is expected to have a suppressive effect on magnetic field effects (MFEs), as is the electron-electron dipolar interaction, and thus both cannot be ignored. Therefore, using the stochastic Schrödinger equation, correlation functions of the dynamics have been deduced for various configurations of diffusion coefficients and hyperfine couplings, a broad survey that has produced more accurate and true-to-life results for the specific case of recombination of two peroxy radicals derived from unsaturated lipids. In addition, making use of Nakajima-Zwanzig equation, the lipid systems under investigation were modelled in the Zeno regime of asymmetrical recombination rates, resulting in MFEs that would have otherwise been unrealisable using a conventional RPM.

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B2-02

Coordination environment of manganese affinity sites in photosystem II measured by ^{14}N HYSCORE

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Photosynthetic protein complex, photosystem II (PSII), performs oxygen evolution in the manganese cluster, which consists of four Mn, one Ca and five O^[1], called a distorted chair structure (Fig. 1). Four Mn ions, labelled Mn1-4, coordinates with different amino-acids. The Mn cluster is deactivated by chemical reduction, however, it is reassembled in the presence of Mn, and Ca ions under light. This is known as photoactivation. The mechanism is still unclear.

Crystal structural analysis suggested an Mn ion was strongly coordinated at the site of either Mn1 or Mn2. The location of the strongly bound Mn ion is not specified. The Mn would have an important role for photoactivation.

We investigated the coordination of the Mn site using pulsed EPR. HYSCORE results showed that the specific Mn was weakly coupled with a ^{14}N nucleus, which was ascribed to the Mn2 site in the native manganese cluster (Fig. 2). The affinity of the Mn site is also measured. These properties provide a model for the photoactivation mechanism.

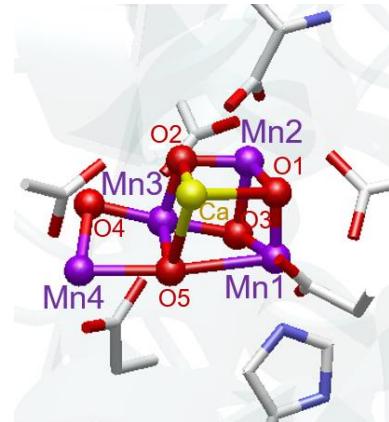


Fig. 1. Structure of the Mn₄CaO₅ cluster in PSII

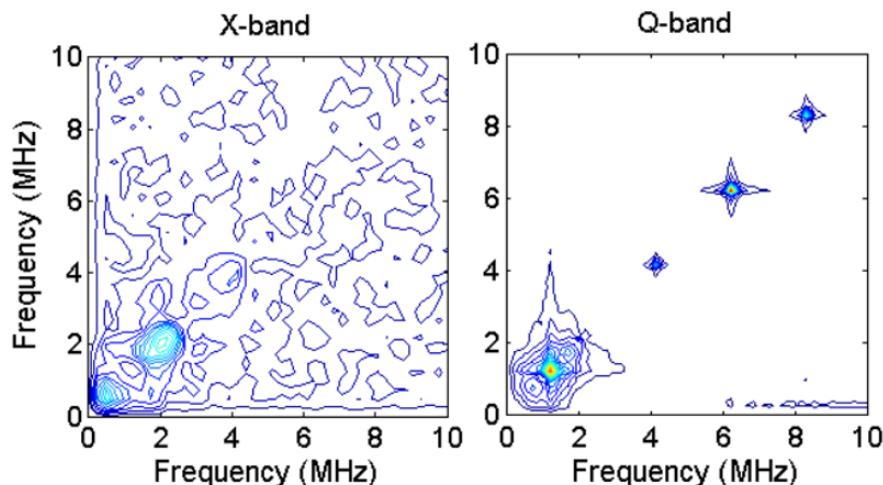


Fig. 2. X, Q-band HYSCORE spectra of the specific Mn²⁺ in the PSII under the reduced conditions.

Reference:

- [1] Umena, Y., Kawakami, K., Shen, JR. et al. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature*, 473, 55–60 (2011).

B2-03

The development of photochemically induced dynamic nuclear polarization dyes for proteins

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It is well known that the function of proteins is closely related to their structures. Consequently, elucidating the protein structures at the molecular level is crucial to understanding protein function. Nuclear magnetic resonance in solution (solution NMR) is a promising method because weak and dynamic interaction can be visualized. However, the application in protein structure analysis using solution NMR is limited due to its inherent low sensitivity. To address this challenge, we focused on nuclear hyperpolarization by photochemically induced dynamic nuclear polarization (photo-CIDNP). Photo-CIDNP enhances NMR sensitivity through a radical pair mechanism (Fig. 1a).^[1] Photo-CIDNP can hyperpolarize several amino acids, indicating a suitable method for protein NMR. However, photo-CIDNP dyes for protein structural analysis are mainly flavin derivatives, which limited applications due to their low photostability.

In this study, we explored novel photo-CIDNP dyes for protein structural analysis. Since protein NMR requires a significant number of scans, photo-CIDNP dyes require high photostability. In this respect, the high photostability of porphyrin derivatives is promising. We chose TMPyP derivatives of the water-soluble cationic porphyrin (Fig. 1b).^[2] Photo-CIDNP for several amino acids (Fig. 1c) was measured to investigate the potential of TMPyP derivatives. The resulting enhancement was considered based on the photophysical properties and spin dynamics. Based on them, photo-CIDNP of proteins was also demonstrated.

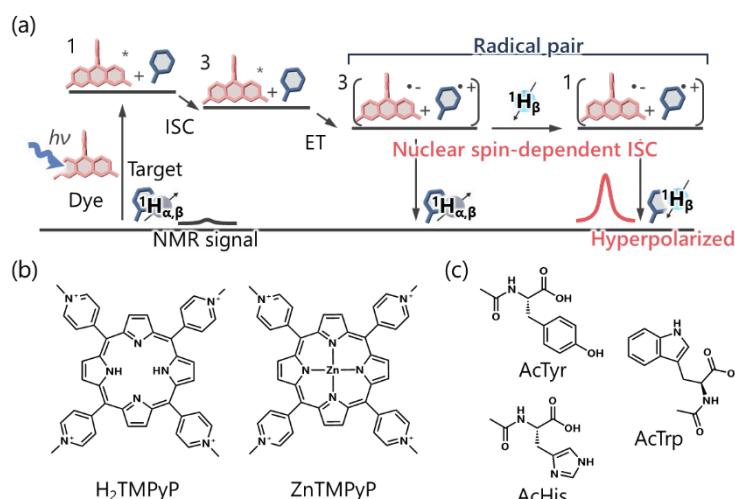


Figure 1. (a) Schematic representation of photo-CIDNP. ISC: intersystem crossing, ET: electron transfer. Chemical structure of (b) TMPyP derivatives and (c) acetyl-protected aromatic amino acids.

References:

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Simulated RYDMR spectra of candidates for magnetically sensitive radical pairs in cryptochrome.

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A wide variety of avian species have a light dependent magnetic compass sense^[1], which could be used during migration for navigation and orientation. The compass sense is possibly based on a radical pair mechanism occurring in the animal's cryptochrome proteins. Although there are extensive studies of cryptochrome's magnetic properties, both experimental and theoretical, the underlying building blocks of the radical pair mechanism are still under discussion. This work simulates reaction yield detected magnetic resonance (RYDMR) spectra of radical pairs theorized to be formed in cryptochrome, in order to guide experimental studies. The explored radical pairs are FAD with tryptophan (FAD-Trp), and FAD with a hypothetical radical with no hyperfine interactions Z (FAD-Z). The simulated RYDMR spectra are used to observe the impact of different magnetic environments on the yields of the reaction products, to understand which properties can be measured using RYDMR experiments. The spectra measure the difference in product yields during a reaction under static fields alone, and under the same static field in the presence of an oscillating field of 0.2 mT either parallel or perpendicular to the static field. The computational simulations of the spin dynamics of the systems were calculated using MolSpin^[2, 3], and the calculations needed to obtain the hyperfine tensors and dipolar couplings of the molecules were done using Orca. FAD-Trp's spectrum shows a more complex structure compared to FAD-Z due to tryptophan's more anisotropic hyperfine interactions.

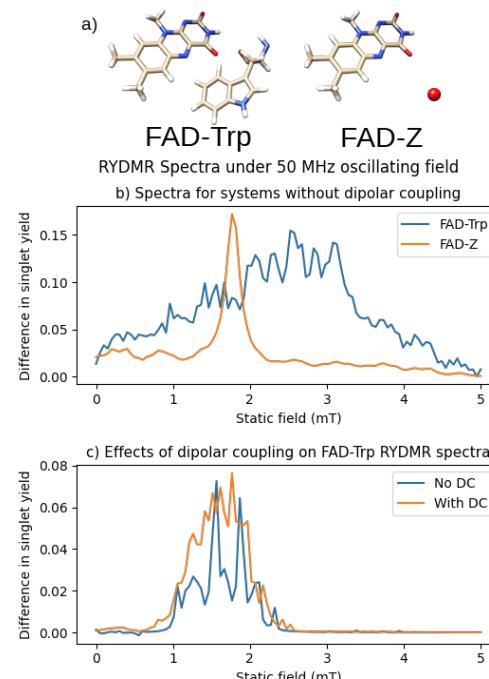


Figure 1. Simulated RYDMR spectrum of singlet yield for radical pair candidates. a) Radical pair candidates. b) Spectrum of all candidates under an oscillating field perpendicular to the static field. FAD-Trp is scaled up by a factor of 5 to highlight the structure. c) Spectra of FAD-Trp under same conditions showing the line broadening caused by the inclusion of dipolar coupling. A reduced number of nuclei were used in this simulation to highlight the effect.

Computational simulations of the spin dynamics of the systems were calculated using MolSpin^[2, 3], and the calculations needed to obtain the hyperfine tensors and dipolar couplings of the molecules were done using Orca. FAD-Trp's spectrum shows a more complex structure compared to FAD-Z due to tryptophan's more anisotropic hyperfine interactions.

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Dynamic spin interactions could enhance magnetic compass sensitivity in cryptochrome radical pairs

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Simulations of magnetic compass sensitivity of radical pairs in cryptochromes face several fundamental challenges. Notably, the anisotropy in the singlet product yield, crucial for the magnetic compass sense, is strongly attenuated when realistic numbers of nuclear spins are incorporated in both radicals^[1]. Molecular dynamics simulations of cryptochromes reveal complex time-dependent spin interactions, leading to spin relaxation processes that could have a beneficial effect on compass sensitivity^[2, 3]. Previous spin dynamics calculations have relied on static spin interactions and phenomenological descriptions of spin relaxation, and consequently have limited relevance. In this study, we employ newly developed computational methods to investigate the way in which realistic, dynamic spin interactions might influence the magnetic compass sensitivity of cryptochrome radical pairs. By systematically examining magnetic fluctuations that impact the underlying spin dynamics, and comparing these motions to real protein dynamics, we gain new insights into potential increases in the reaction-yield anisotropy.

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B2-06

Insights into the Structure of the S₂ High Spin State of the Mn Cluster in Photosystem II by electron paramagnetic resonance (EPR) spectroscopy

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Photosynthetic oxygen evolution occurs when the Mn cluster in the photosystem II protein complex oxidizes water. X ray crystallography revealed that the Mn cluster has a ‘distorted chair’ structure consisting of four Mn, one Ca, and five O (Mn_4CaO_5) : Fig. 1^[1]. The Mn_4CaO_5 cluster transitions through five intermediate states S_i ($i = 0-4$) to oxidize water and generate oxygen. In particular, the S_2 state has been studied using electron paramagnetic resonance (EPR) techniques. X-band (~ 9.5 GHz) CW-EPR spectrum revealed that the S_2 state has two isomers ($S = 1/2$ and $S = 5/2$). XFEL experiment showed that the $S = 1/2$ state has an open cubane structure. The structure corresponding to the $S = 5/2$ is unclear. Besides, another S_2 state isomer with a $S = 7/2$ was observed during the relaxation process from the S_3 state to the S_2 state. There is a possibility that the high spin state, the $S = 5/2$ state or the $S = 7/2$ state, works as an intermediate state during the $S_2\text{-}S_3$ state transition: Fig. 2. Understanding the intermediate state is crucial for elucidating the oxygen evolution mechanism.

In this work, multi-frequency EPR, X-band (~9.5GHz), and Q-band (~34 GHz) measurements are performed to characterize the S_2 state high spin structures. We measured the field-swept spectra in X-band and Q-band of the two high spin states. As the results, the structural parameters, that is, zero field splitting D and E , were determined for these states. Furthermore, the excitation energies ΔE of the ground states for the $S = 5/2$ and $S = 7/2$ states were estimated from the spin lattice relaxation time T_1 . By comparing with quantum chemical calculations, we discuss the possible structures of the S_2 high spin state.

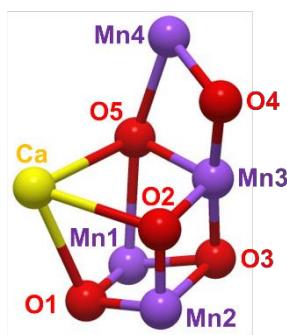


Figure 1. Structure of the Mn_4CaO_5 cluster. Purple, yellow, and red spheres represent Mn, Ca, and O, respectively.

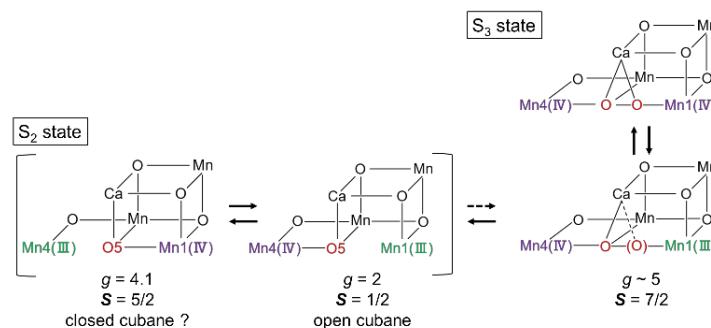


Figure 2. Model for the transition mechanism of S_2 to S_3 states.

References:

- [1] Umena Y. et al., *Nature*, 2011, **473**, 55-60.

B2-07

EPR and SAXS studies of the magnetic field effects of iron-sulfur cluster assembly 1 with mononuclear iron

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Many varieties of animals can sense the geomagnetic field and use it as a compass. Migratory birds utilize their ability of magnetoreception for migration. Although the mechanism of magnetoreception is still unclear, cryptochromes have been suggested as a quantum sensor of the magnetic field. However, the partner of cryptochromes has not yet been identified. It has been proposed that pigeon ISCA1 (clISCA1) plays a role in magnetoreception through interaction with cryptochromes^[1]. Iron-sulfur (Fe-S) cluster assembly 1 (ISCA1) is a protein conserved in a variety of organisms. clISCA1 exhibits two different iron-sulfur clusters, [2Fe-2S] and [3Fe-4S]^[2,3], and mononuclear iron. The magnetic properties of ISCA1 depend on which of these clusters are formed. It has been reported that the oligomerization of clISCA1 is induced by a magnetic field, as shown by small-angle X-ray scattering (SAXS)^[4]. Whether this unique property is commonly conserved in other species, especially human ISCA1 (hsISCA1), is unknown. Recent studies have also shown that clISCA1 binds not only Fe-S clusters but also mononuclear iron of unknown function, suggesting that clISCA1 may be endowed with some magnetic properties.

In this study, electron paramagnetic resonance (EPR) revealed that hsISCA1 also binds mononuclear iron atoms. Furthermore, the structural properties and magnetic response of Fe-S cluster-free ISCA1 (Fe-ISCA1), which binds only mononuclear iron, were investigated for pigeons (Fe-clISCA1) and humans (Fe-hsISCA1) by SAXS analysis. The results showed that both Fe-clISCA1 and Fe-hsISCA1 responded to external magnetic fields, but their oligomeric structures and molecular behaviors were different. Upon application of an external magnetic field (about 180 mT), the columnar oligomers of Fe-hsISCA1 rapidly shortened within 1 min and gradually elongated again after 10 min (Figure 1). This result indicates that mononuclear iron atoms contribute to the basis of the magnetically induced superordered structuring of ISCA1. On the other hand, the contribution of Fe-S clusters to ISCA1 columnarization varies among species, and although the physiological role of the magnetic properties of ISCA1 is not yet fully understood, this study demonstrates that the magnetic field responsiveness of ISCA1 is conserved in humans. Magnetic field responsiveness may be a hidden fundamental property of ISCA1 that is retained even when the Fe-S cluster is released.

References:

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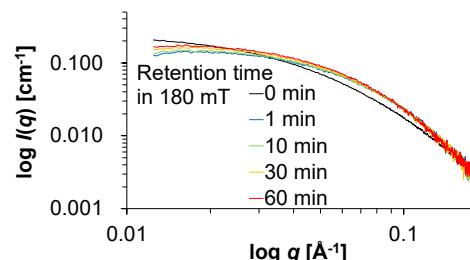


Figure 1. Results of SAXS analyses for hsISCA1 in 180 mT magnetic field.

Elucidation of radicals in Animalia cryptochrome by EPR

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Cryptochromes are blue-light photoreceptor proteins found in the retinae of birds, and proposed to be the key to magnetoreception in night-migratory songbirds.^[1] Upon photoexcitation of a non-covalently bound flavin cofactor within the protein, a chain of electron transfer processes occur across nearby tryptophan residues, with the flavin cofactor acting as the initial electron acceptor. The electron transfer cascade generates a spatially separated, spin-correlated, radical pair between the flavin and a tryptophan residue. The spin correlation is due to the initially generated singlet radical pair not being an eigenstate of the total spin Hamiltonian. Subsequent singlet-triplet mixing, driven by hyperfine couplings in the radical pair, is sensitive to external magnetic fields and therefore may invoke magnetosensitivity on the yields and rates of downstream chemical species and processes.

A vast array of EPR and optical spectroscopy techniques have been used to investigate cryptochrome proteins.^[2] EPR plays a particularly important role in the identification of radicals which often overlap in their absorption spectra: the residues that constitute the field-dependent spin-correlated radical pairs, and any downstream radicals that may act as signalling states for magnetoreception. For the identification of radical pairs, out-of-phase electron spin echo envelope modulation (out-of-phase ESEEM) and transient EPR (trEPR) techniques are employed. Out-of-phase ESEEM, a pulsed EPR experiment, probes the inter-electron spin couplings between the constituent radicals in the radical pairs. From the distance-dependence of the dipolar coupling, the separation between radicals can be determined. Continuous-wave (cw)EPR spectra recorded via trEPR, on a ns-μs timescale, are influenced by these inter-electron spin couplings as well as a number of other parameters, such as the g-values and hyperfine couplings of each constituent radical, and the relative orientations and positions of the two radical species in space. A home-written simulation routine is used to fit many of these parameters to confirm the precise identities of each radical pair.

To investigate the formation of stable cryptochrome radicals, that live on the timescale of hours and above, cwEPR and electron nuclear double resonance (ENDOR) techniques are used to identify radicals via their g-values and ¹H hyperfine couplings. In this work, wildtype and single-point mutated proteins have been studied for a range of Animalia cryptochromes, to unambiguously identify and characterise any radicals formed therein.

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Magnetic field effects on a singlet-born radical pair embedded in vesicle capsules towards quantum dynamic therapy

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We propose “quantum dynamic therapy (QDT)”, which is a Drug Delivery System that enables drug release from a nanocapsule by light irradiation and magnetic control of the release efficiency. It is expected that the release efficiency is reduced by applied magnetic field if a singlet-born radical ion pair is embedded in a nanocapsule. In this study, we have developed a donor-acceptor embedded vesicle capsule and evaluated magnetic field effect (MFE) on the radical pair dynamics.

Vesicle capsules were created in the phosphate buffer (pH 7.4) by the ethanol injection method using Tween 40 (10 mM) as a nonionic surfactant and cholesterol (3 mM) as a stabilizer (Figure 1a and b). A phenothiazine derivative MEEPT (2 mM) was used as a donor, and Tp-PDI (20 μ M) was used as an accepter dye because its intersystem crossing yield is negligible (Figure 1c and d). Nanosecond transient absorption were measured using pulsed Nd:YAG laser (532 nm) and CW Xe lamp as excitation and probe light sources, respectively.

The fluorescence from the accepter dye is significantly quenched by addition of the donor. This indicates highly efficient photoinduced electron transfer from the S_1 state of the accepter (quantum yield of ~95%). Figure 2 shows the transient absorption kinetics for the donor-accepter embedded vesicle capsule. The fast decay of the radical anion at ~10 ns is assigned to geminate recombination of the radical pair, and the long-lived ($>\mu$ s) radical is observed at later times. The yield of the long-lived radical is decreased by 11% upon application of external magnetic field of 250 mT. It is considered that the spin state mixing from the singlet radical pair to the triplet radical pair is prohibited under a magnetic field, which promotes recombination and reduces the yield of dissociated long-lived radicals. MARY spectrum for the yield of the long-lived radical exhibits a half-magnetic field ($B_{1/2}$) of 4 mT, indicating that MFE is due to the hyperfine mechanism (Figure 3). Currently, we are evaluating the release efficiency by encapsulating a hydrophilic dye instead of a water-soluble drug. Experimental details will be presented.

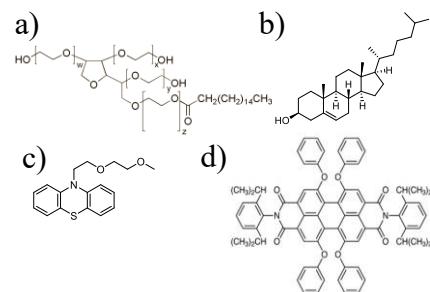


Figure 1. Chemical structures of a) Tween40, b) Cholesterol, c) MEEPT (Donor), and d) Tp-PDI (Acceptor).

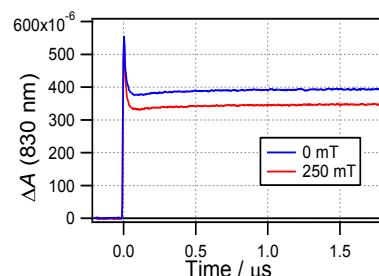


Figure 2. MFE on kinetic traces of transient absorption due to Tp-PDI radical anion. Excitation wavelength is 532 nm.

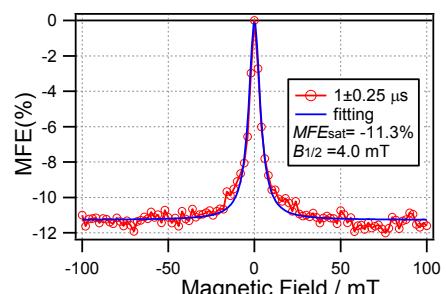


Figure 3. MARY spectrum.

Currently, we are evaluating the release efficiency by encapsulating a hydrophilic dye instead of a water-soluble drug. Experimental details will be presented.

B2-10

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Poster: Angular Precision of Radical Pair Based Avian Magnetoreception

Abstract: This work attempts to explain in theory why the radical pair based avian magnetic compass is capable of sensing the earth magnetic field to an extremely high precision even when the bird flies at night under extremely low light intensities. I will demonstrate how to strictly evaluate the expected error in the bird's perceived direction of the earth magnetic field, and elaborate on how small this error can be made.

B2-11

Difference of the Spin mixing in low magnetic field in the system of xanthone-DABCO and thionine-DABCO in SDS micellar media.

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This poster discusses the relationship between the low field effects (LFEs) and the coherent spin dynamics comparing the spin dynamics in the xanthone-DABCO (1,4-diazabicyclo[2.2.2]octane)[1] and thionine-DABCO[2] systems. Both systems undergo photoinduced electron transfer reactions, forming radical pairs with similar hyperfine structures. Both systems also show similar low-field effects. Here, the spin dynamics in the low-field regime are investigated using switching of external magnetic field (SEMF) experiments with two different pulse schemes. Fig. 1(a) and 2(a) show the time dependence of the field switching from the peak of the LFE to the high field (we call it *forward switching*) in each system. The decay of forward field switching reflects the lifetime of the radical pairs before switching in low fields. In contrast, switching from the peak of the LFE to zero field (*reverse switching*) in Fig. 1 (b) gives a decay with a very short time constant. However, in thionine-DABCO system, the reduction of the lifetime is limited as shown in Fig. 2 (b). Theoretical considerations are still ongoing, but in principle, if coherent LFEs due to splitting of degenerate states [3] dominate, the short decay time constant is about half reciprocal of the Zeeman energy. In conclusion, the inverse field-switching method may be useful for diagnosing the presence of coherent spin dynamics causing LFEs.

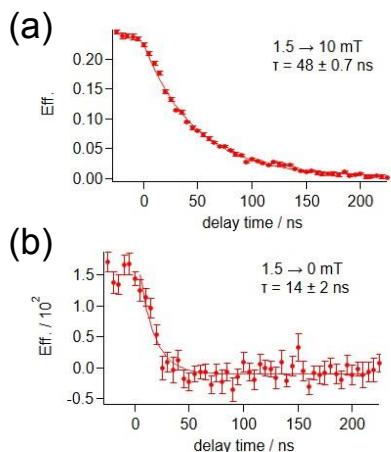


Figure 1. SEMF in Xanthone-DABCO

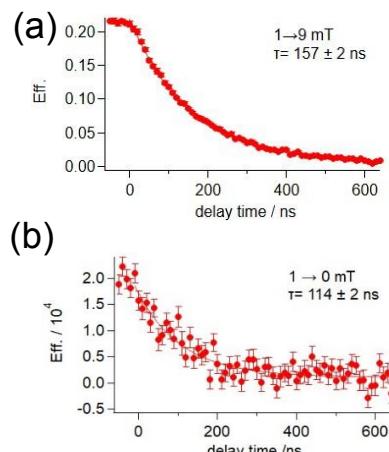


Figure 1. SEMF in Thionine-DABCO

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B2-12

Exploration of molecular candidates for biomedical applications of microwave-free-driven hyperpolarization technology

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Magnetic Resonance Imaging (MRI) has become indispensable in modern medical diagnostics. However, its poor sensitivity remains as a significant challenge. One solution to this problem is the generation of a hyperpolarized state, wherein the distribution of nuclear spins is non-thermally distributed. One of the hyperpolarization techniques is photo-chemically induced dynamic nuclear polarization (Photo-CIDNP) based on the radical pair formation involving a dye (D) and a quencher molecule (Q) upon light irradiation. Photo-CIDNP achieves polarization without the need for microwaves and operates in aqueous solvents, offering superior biocompatibility.

Representative dyes for Photo-CIDNP including flavin mononucleotide and fluorescein derivatives have been extensively used for MRI sensitivity enhancement. However, these dyes absorb light in the blue to green spectral region, necessitating the development of dyes that absorb in the near-infrared (NIR) region, known as the "biological window," for effective *in vivo* MRI applications.

In this study, we have focused on the development of NIR-absorbing dyes for Photo-CIDNP. The results of our exploration of various chromophores will be presented.

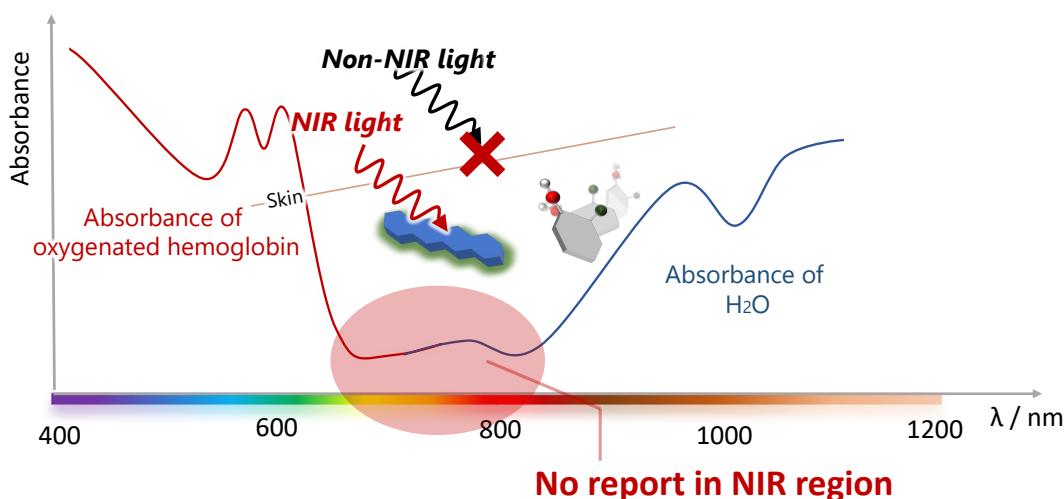


Figure 1. Concepts for Photo-CIDNP driven by NIR light

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C2-01

Transient EPR Study of Intramolecular Singlet Fission in Tetracene Oligomers

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Singlet fission is a photoreaction process that generates two excited triplet excitons from one excited singlet exciton, and it is promised to have applications in solar cells for efficient photo-energy conversion and in quantum information science using entangled triplet pairs. We have observed photoelectric charge separation and singlet exciton splitting processes in various systems, and have developed a theoretical analysis method for generating electron spin polarization through spin polarization transfer [1-2]. In this study, we have observed singlet fission in tetracene hexamer covalently linked by biphenyl chain by using a transient EPR method. The structures and spin polarization generation process of the quintet multiexcitons and dissociated excitons were analyzed using the obtained spectra.

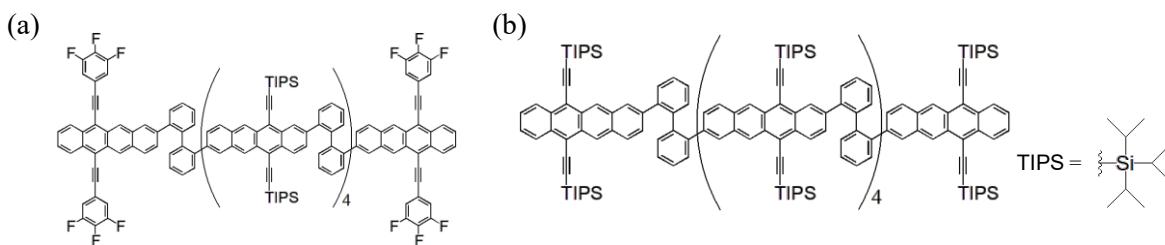


Figure 1. Chemical structures of tetracene oligomers used in this study.

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C2-02

EPR in the high-cooperativity regime: a playground for microwave quantum electronics

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Quantum electronics operating in the microwave domain, e.g. quantum amplifiers/oscillators, are becoming essential building blocks of quantum computers, sensors and communication devices due to their ultralow (i.e. quantum-limited) noise performance. However, to maintain the delicate quantum coherence and non-equilibrium quantum states, microwave quantum electronics have long been imprisoned in refrigerators. The last decade has seen the dawn of solving the dilemma by the EPR-assisted discovery^[1,2] of the optically pumped electron spins in solids that possess long spin relaxation times and high polarization at room temperature. By coupling the spins to microwave cavities with high cooperativity, several works^[3,4,5] have demonstrated the feasibility of such hybrid quantum systems to be configured as room-temperature microwave quantum electronics while the functionalities and controllability are still lacking of exploration.

In this talk, we will report on a solid-state hybrid quantum system, constituted by the optically polarized pentacene triplet spins coupled to a high- Q sapphire cavity, that for the first time serve for quantum amplification and oscillation at X band (~ 9.4 GHz) via the masing process at room temperature. In particular, the performance of the device and the constituent parts can all be evaluated and optimized by the EPR techniques. Our work^[6] demonstrates the powerfulness and full compatibility of EPR spectroscopy for facilitating the development of microwave quantum electronics at room temperature.

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Magnetic Field Effects on Photocatalytic Dimerization Reactions of Anthracene Derivatives due to Triplet-Triplet Annihilation in Cyclodextrin Complexes

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Photon upconversion based on sensitized triplet-triplet annihilation (PUC-TTA) has attracted attention in the fields of next generation solar cells such as dye-sensitized, organic, and perovskite solar cells and photocatalysis. Previously, we found that the efficiency of PUC-TTA using platinum (II) octaethyl-porphyrin as a triplet photosensitizer and 9,10-diphenylanthracene as a fluorescent emitter enlarged using localized surface plasmon resonance of metal nanoparticles.^[1] Also, we found the positive magnetic field effect (MFE) on PUC-TTA, where the upconverted fluorescence from an emitter is strengthened in the presence of a magnetic field in PtOEP-DPA system in toluene solution at high concentration of DPA.^[2]

In present study, as an application of the PUC-TTA, we have examined the influences of cyclodextrin (CD) and magnetic field on photocatalytic dimerization of anthracene derivatives through TTA were examined in platinum (II) porphyrin derivative (PtTCPP) - anthracene derivative (9-AnC) system in buffer aqueous solution with and without CD (Fig. 1).

The results of absorption spectra and ¹H NMR spectra indicate that the photocatalytic dimerization reactions operating with visible light (532 nm) of PtTCPP - 9-AnC systems with and without CD were achieved though TTA. The rate of photocatalytic dimerization reaction varied by type of CDs (α -, β -, and γ -CDs) and the presence of magnetic field (Table 1). No MFEs on the direct photodimerization reaction of 9-AnC operating with ultraviolet light. Therefore, the MFEs are responsible for TTA process.

We will discuss the effects of CD and magnetic field on the photocatalytic dimerization of 9-AnC though TTA including stereoselectivity of dimer photoproducts.

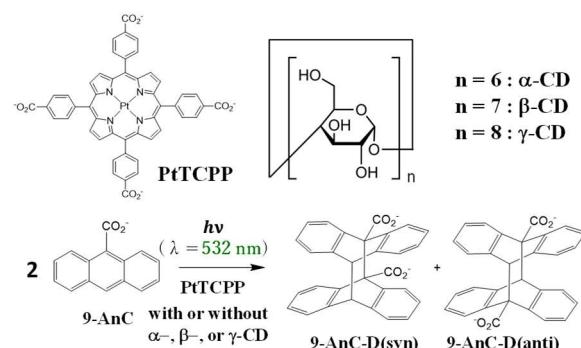


Fig. 1. Reaction scheme of photocatalytic dimerization of 9-AnC due to TTA in PtTCPP - 9-AnC systems in buffer aqueous solution with and without CD upon laser irradiation (532 nm).

Table 1. MFEs on k_{PD} -values(min⁻¹) in PtTCPP-9-AnC system with and without CD

	0.0 T	0.5 T
PtTCPP-9-AnC	1.61×10^{-2}	1.47×10^{-2}
PtTCPP-9-AnC- α -CD	3.02×10^{-2}	2.35×10^{-2}
PtTCPP-9-AnC- β -CD	1.28×10^{-2}	2.01×10^{-2}
PtTCPP-9-AnC- γ -CD	1.82×10^{-2}	2.26×10^{-2}

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C2-04

Donor-acceptor molecular systems derived from π -extended porphyrins and C₆₀

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Photo-induced charge separation (CS) and charge recombination (CR) play crucial roles in light-to-energy conversion in nature and in artificial light conversion systems used for photovoltaics, photosynthesis, and photocatalysis. High CS efficiency and long-lived CS state are critical to realizing efficient solar energy conversion.^[1-3] In this presentation, novel donor-acceptor systems derived from π -extended porphyrin as the donor and C₆₀ as the acceptor through ligand coordination strategies will be presented. An exceptionally long-lived charge separation (CS) state (37.4 μ s) was established with the benzoimidazo-isoindole-fused porphyrins and C₆₀ (Figure 1, A).^[4, 5] The exceptionally long-lived CS state was attributed to the formation of ³CT through spin-orbit charge transfer intersystem crossing (SOCT-ISC), which suggest the existence of a new mechanism paradigm for CS and charge combination (CR) dynamics/kinetics/thermodynamics.

Porphyrin oligomers including dimers and trimers based on benzoimidazo-isoindole-fused porphyrins have also been prepared (Figure 1, B & C). While ZnD1-C₆₀ exhibited long-lived CS state (~30-40 ms), ZnFBD1 system displayed efficient singlet-singlet energy transfer (>95% efficiency).^[5] Interestingly, no charge separation in ZnFBD1-C₆₀ system was observed wherein excitation transfer dominated the process. Different scenario occurred in the trimer system. Zn-Trimer-1 showed strong exciton coupling and titration of Zn-rimer-1 with C₆₀ suggested cooperativity of the three porphyrin components, which is in sharp contrast to that was observed with ZnD1-C₆₀ system. These results showcase the significant impact of heteroatom/heterocycles and the importance of the conjugated π -spacer in governing the energy and electron transfer events.^[6, 7]

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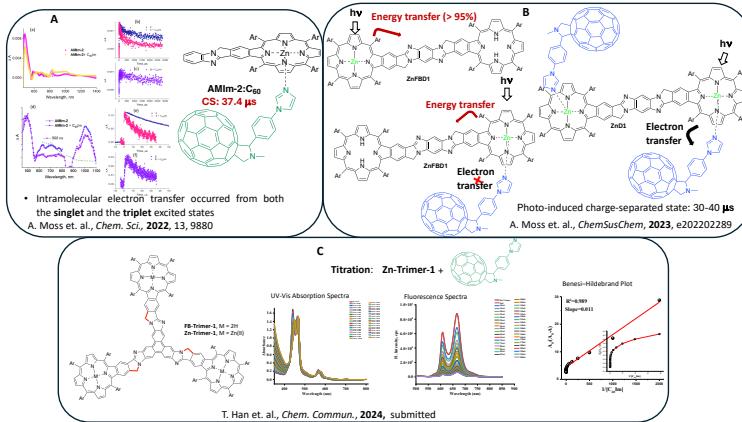


Figure 1 Benzoimidazol-isoindole-fused porphyrins. A: Monomer, B: Dimer, C: Trimer.

C2-05

Radical Spin Polarisation and Magnetosensitivity from Reversible Doublet-Triplet Energy Transfer

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Molecular doublet ($S = 1/2$) and triplet ($S = 1$) spin states provide potential building units for designer material platforms towards quantum information science (QIS) and spintronic applications. The challenge is to devise useful photon-spin mechanisms that can take advantage of the excellent optical and spin properties promised by π -conjugated organic materials. Here we set out a framework for establishing magnetosensitive luminescence and spin polarisation for systems with reversible energy transfer between doublet and triplet states.^[1] Highlighting the dependence of the photon-spin mechanism on the magnitude and sign of the exchange interaction between doublet and triplet spins, we outline potential applications of radical-triplet systems towards magnetic field inclination sensing. Reversible doublet-triplet energy transfer in inter- and intramolecular radical-acene systems is then demonstrated, with measurements of the magnetosensitivity of doublet emission and polarisation to interrogate the interactions of triplet and doublet species. Through theory and experiment, our results reveal the opportunities for radical-triplet systems towards the design of functional molecular materials.

Grant funding: EPSRC (EP/W018519/1, EP/Y002555/1), Royal Society (URF/R1/201300)

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C2-06

Quantum phase difference estimation: A quantum algorithm for the direct calculation of energy differences and application to singlet–triplet energy gap

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Quantum computing is one of the hottest areas of research in modern science. Among the various topics in quantum computing, sophisticated quantum chemical calculations of atoms and molecules are considered to be one of the most promising applications of quantum computers. A quantum phase estimation (QPE) algorithm^[1,2] is able to compute the eigenfunctions and corresponding eigenvalues of a unitary operator by using measurements to project an approximate wave function onto the eigenfunction of the Hamiltonian.

It is worth noting that most chemical problems relevant to quantum chemical calculations deal with energy differences between different electronic states or geometries, rather than total energies themselves. In particular, in the field of spin chemistry, calculating the spin state energy gaps to find the ground state spin state is an important application of quantum chemical calculations.

Since quantum computers can use quantum superposition states as their computational resources, it is possible to compute energy differences between two states directly without calculating the total energies of individual electronic states on a quantum computer.^[3–6] Here we propose a quantum phase difference estimation (QPDE) algorithm, a general quantum algorithm for the direct calculation of energy gaps.^[6] The QPDE algorithm uses a quantum state in the superposition of two electronic states whose energy gap is of interest. By using the quantum superposition of low-spin and high-spin states, we are able to compute the spin-state energy gap directly. As a proof of concept demonstrations, we report numerical experiments for the singlet–triplet energy differences of the hydrogen molecule.

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C2-07

Spin-optical transitions of π -radicals towards enhanced photon upconversion

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Triplet annihilation of excitons to higher energy singlet states enables molecular upconversion of low to high energy photons with applications in photonics, optoelectronics, photocatalysis and imaging. Upconversion initiated by closed-shell molecules leads to reduced energy shift with loss from the singlet-triplet energy gap of the sensitiser. Here we explore open-shell organic radicals as sensitisers that maximise the energy shift of photon upconversion. Our design combines optical transitions from a triphenylmethyl radical component with energy-degenerate triplet states of an anthracene-based annihilator in one molecule. Following photoexcitation the radical forms a manifold of doublet and quartet states with extended excited state lifetime and direct channels for sensitisation of annihilator molecules. Red-to-blue photon upconversion was demonstrated in solution with anthracene derivatives showing up to 0.96 eV energy shift. Understanding the exciton nature and design rules for spin-optical properties of the radicals could improve designs for upconversion and energy management in molecules beyond singlet and triplet excitons.

This work is funded by the EPSRC (EP/W018519/1)

RadicalPy: democratising spin dynamics simulations for the experimentalist

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In this study, we describe our software for the field of spin chemistry, spintronics, and quantum biology, which is built around radical/triplet pairs and similar phenomena. *RadicalPy*¹ is written in the widely used Python programming language, which is accessible to academics at various stages, i.e., from first-year undergraduates to seasoned professors. We have provided detailed and intuitive documentation that describes the methodology and provides references to the user (<https://radicalpy.readthedocs.io/>). The software is open-source and is easily installed with a simple pip command. *RadicalPy* is also freely available to use on Windows, Mac, and Linux, accommodating the users OS of choice. Furthermore, unlike existing software,² *RadicalPy* is written by a spin chemist and computer scientist, providing accurate, efficient, and intuitive software for the user. The software also offers a database of molecules, which alleviates the need for complex DFT calculations, a technique that chemists or biologists may not be familiar with.

RadicalPy also includes classical and semi-classical³ simulation methodologies, which are not present in the existing software, as they focus on pure quantum magnetic resonance simulations.^{2a,b} The inclusion of these techniques has allowed us to develop a new simulation method, which we name kine-quantum. The new technique allows us to simulate spectral and temporal experimental data with unprecedented precision and speed. While the runtime of pure quantum methods inflates exponentially with the number of particles (1 hour for $N=6$ particles) with the results still not matching the experimental data, the kine-quantum method's runtime is independent of the number of particles and the same system can be simulated in a constant 20 seconds with high accuracy (Fig. 1).

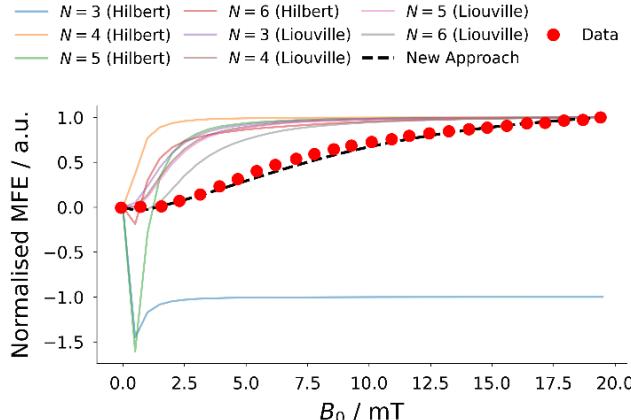


Figure 1. Accuracy test for MARY simulations with increasing number of spins. The experimental result was unsuccessfully simulated in all pure quantum simulations. The experiment was successfully modelled with the new kine-quantum approach.

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Supported by JST PRESTO (Quantum Bio) Grant No. JPMJPR19G1 (L.M.A.) and Grants-in-Aid for Scientific Research (KAKENHI), Early-Career Scientists Grant No. 22K17900 (E.V.).

C2-09

Optimality out of Adversity? Enhancing Magnetic Field Effects through Strong and Persistent System-Environment Interaction

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The Radical Pair Mechanism (RPM) posits that the coherent spin dynamics of electrons in radical intermediates facilitate sensitivity to magnetic fields. Studies have suggested that the RPM might underpin numerous magnetosensitive traits in biology [1], such as the ability of some organisms to sense the weak geomagnetic field ($\sim 50\mu\text{T}$). We have recently demonstrated that radical pairs in close contact, such as the FAD-superoxide radical pair, can achieve sensitivity to magnetic fields via the quantum Zeno effect, despite strong inter-radical coupling, provided the recombination reaction is asymmetric. However, strong inter-radical coupling is likely to be accompanied by significant system-environment interaction, believed to diminish sensitivity, due to fluctuations in the inter-radical distance. By comparing to numerically exact methodology, the Hierarchical Equations of Motion (HEOM), I will show that for strong and persistent fluctuations in the inter-radical coupling, the magnetosensitivity can be further enhanced at a failure point in a Markovian limit Nakajima-Zwanzig approach [2]. This highlights an observation that enhancements can be found despite conditions previously thought to be adverse. In line with this I will discuss how radical motion [3, 4] can enhance sensitivity and question the optimality of the RPM in the limits of realistic model complexity [5, 6].

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C2-10

Study of the electronic structure of a β -diketiminate manganese hydride dimer catalyst

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The electronic structure of a dimeric manganese hydride catalyst supported by β -diketiminate ligands, $[({}^{2,6\text{-iPr}_2\text{Ph}}\text{BDI})\text{Mn}(\mu\text{-H})]_2$, was investigated using electron paramagnetic resonance (EPR) spectroscopy, superconducting quantum interference device (SQUID) magnetometry and density functional theory (DFT). A triple bond between the manganese centres was anticipated from simple electron-counting rules; however, calculations revealed Mn–Mn Mayer bond orders of 0.21 and 0.27 for the ferromagnetically-coupled and antiferromagnetically-coupled extremes, respectively. In accordance with experimentally determined Heisenberg exchange coupling constants of $-15 \pm 0.1 \text{ cm}^{-1}$ (SQUID) and $-10.2 \pm 0.7 \text{ cm}^{-1}$ (EPR), the calculated J_o value of -10.9 cm^{-1} confirmed that the ground state involves antiferromagnetic coupling between high spin Mn(II)-d⁵ centres. The effect of steric bulk on the bond order was examined via a model study with the least sterically-demanding version of the β -diketiminate ligand and was found to be negligible. Mixing between metal- and β -diketiminate-based orbitals was found to be responsible for the absence of a metal–metal multiple bond. The bridging hydrides give rise to a relatively close positioning of the metal centres, while bridging atoms possessing 2p orbitals result in longer Mn–Mn distances and more stable dimers. The synthesis and characterization of the bridging hydroxide variant, $[({}^{2,6\text{-iPr}_2\text{Ph}}\text{BDI})\text{Mn}(\mu\text{-OH})]_2$, provides experimental support for these assessments.

Funding: Institute for Basic Science (IBS-R10-A1), National Science Foundation (Grant No. 1651686) and US Army Research Office (Grant No. W911NF-20-1-0091).

C2-11

Towards strong and long-lived spin polarisation in photoactivated organic molecules for spin-based quantum sensors

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Certain organic chromophores are emerging as promising candidates for a range of photoactivated quantum technologies including ultra-low noise room temperature microwave amplification and magnetic field sensing.[1,2] In such systems, sensing relies on the stimulated collapse of a spin-polarised state or on monitoring the spin coherence of paramagnetic states. However, due to inefficient spin dynamics, the molecular materials underpinning these technologies exhibit limited sensitivity and require strong light sources and high-quality factor resonators. For these families of molecular quantum sensors to be widely applied we must develop new materials with enhanced spin dynamics that simplify their operation and improve sensitivity.

To tackle these issues, we have designed novel approaches to tune the quantum properties of candidate molecular systems and investigated several triplet and radical-based materials capable of producing strong and long-lived electron spin polarisation through intersystem crossing, singlet fission, or radical-triplet interactions.[3–5] Using a combined approach employing optical spectroscopy and transient and pulsed electron spin resonance, it has been possible to link their electronic behaviour with their spin dynamics and, ultimately, determine their merit in quantum sensing applications.

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Acknowledgements: This work was supported by the UK Engineering and Physical Science Research Council through grants EP/V048430/1, EP/W027542/1, and EP/P030548/1.

Light-induced EPR investigation of Y₃N@C₈₀

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The potential for endohedral fragments in metallofullerenes to be controlled by light represents an attractive strategy for the design of photoswitchable molecular machines [1, 2]. It is well established that fullerenes exhibit highly efficient S1/T1 intersystem crossing, resulting in a long lived triplet state with a quantum yield of almost 100% upon photoexcitation. Our interest in such a system is related to its potential to store the quantum information as electron and nuclear spin coherence, and the presence of the endohedral fragment expands the spin states available for manipulation by applying microwave and radiofrequency pulses.

In this work, we studied the endohedral fullerene Y₃N@C₈₀ [1] by light-induced EPR at X- and Q-bands. The figure shows the Fourier transform spectrum of the three-pulse ESEEM (Electron Spin Echo Envelope Modulation) signal. The inset shows the echo detected EPR spectrum recorded during continuous laser excitation at 532 nm (90 mW), and the magnitude of the magnetic field used for the ESEEM measurement is indicated by the star. The Fourier transform spectrum shows two frequencies corresponding to the hyperfine interaction with yttrium nuclei ⁸⁹Y (~1.8MHz) and the Larmor precision of the carbon isotope ¹³C (3.7MHz). It was found that the generation of nuclear spin coherence depends significantly on the magnitude of the external magnetic field. The details of the ESEEM data will be discussed in the presentation.

The research was funded by RSF (project #22-43-04424). The yttrium metallofullerene was provided by Dr. A. Popov, IFW Dresden, Germany.

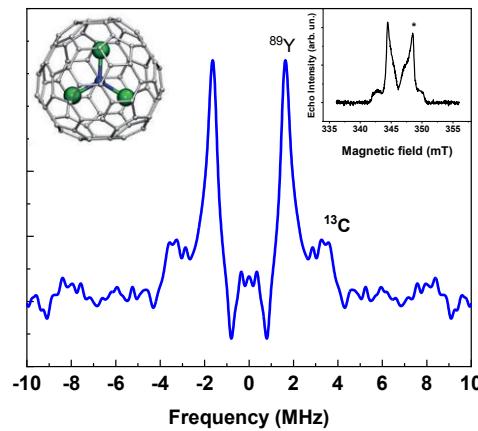


Figure 1. Fourier transform spectrum of the 3-pulse ESEEM of Y₃N@C₈₀ in decalin at a concentration of 0.2 mmol/l. The structure of the molecule is shown on the left, with the green and blue spheres representing the yttrium and nitrogen ions, respectively. The inset shows the echo detected EPR spectrum. The star indicates the position of the magnetic field used for the ESEEM experiment.

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Electron Spin Polarization of an Emissive Diradical with a Triplet Ground State

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Quantum sensing, which utilizes quantum effects to measure physical quantities in external environments, has been attracting significant attention as a highly sensitive measurement technique. Optically detected magnetic resonance (ODMR) using NV centers, which allow for optical initialization by photocycle and readout of spin states, has been studied as a promising method for measuring magnetic, temperature, and electric fields. However, the precise positioning of lattice defects in NV centers is challenging, resulting in limitations in interaction control and scalability^[1, 2].

Therefore, in this study, we focus on organic molecule-based quantum sensors as alternatives to NV centers, aiming for easier control over structure and properties, and designed TTM-type diradical **1**, which is expected to possess a triplet ground state essential for effective initialization via optical cycle and exhibit emission properties, similar to NV centers.

The synthesized diradical **1** is relatively stable and could be purified using GPC. SQUID measurements confirmed diradical **1** has a triplet ground state, while optical measurements revealed its luminescent properties. Furthermore, time-resolved ESR measurements demonstrated its capability to generate electron spin polarization essential for forming initialization states similar to NV centers.

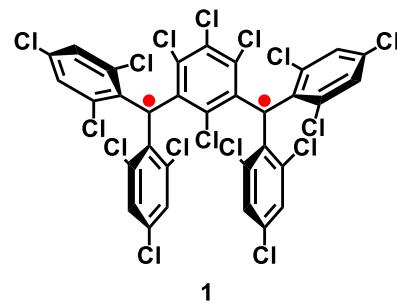


Figure 1. Molecular structure of triplet diradical **1**.

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Portable diamond maser for quantum sensing with 1 Kelvin noise temperatures, without cryogenics

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Masers, the microwave analogue of the laser, can amplify the weakest electrical signals which would allow them to revolutionize medical diagnostics and mobile communications. Previous studies explored them as low noise amplifiers in sensing^[1] and cryogen-free noise reduction through absorbing thermal photons^[2]. However, to this day continuous-wave masers are still trapped in specialist laboratories due to requiring large electromagnets, cryogenic cooling, and vacuum chambers.

We present the first room-temperature continuous-wave maser that can be transported easily out of the laboratory and onto the benchtop. The device uses an NV⁻ diamond gain medium that has been manufactured with isotopic purity to achieve significantly longer coherence times that allow it to sustain masing under more compact and less uniform magnet systems (Fig 1.). We then provide further avenues towards miniaturization through developing methods to manipulate the magnetic field dependence of the gain material with angular orientation.

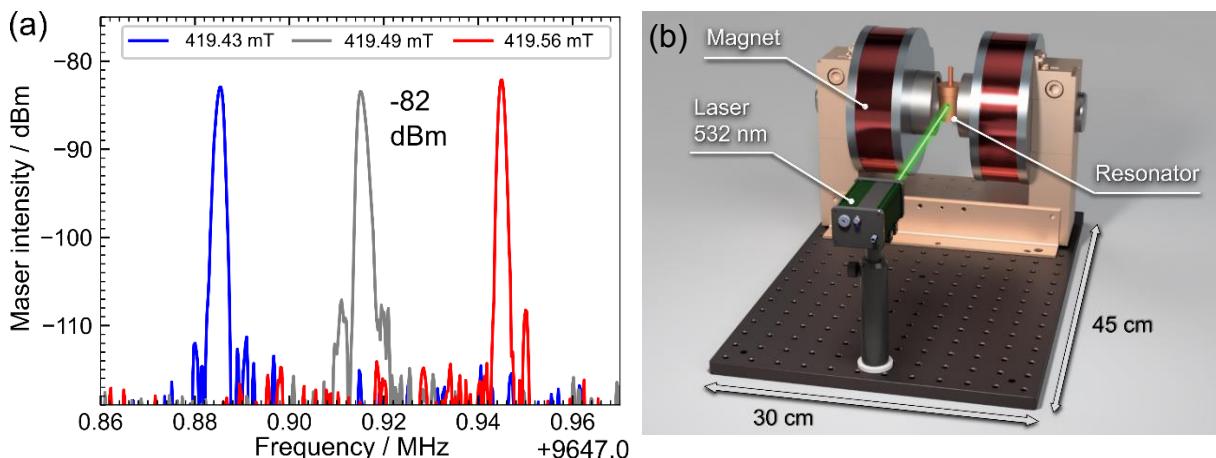


Figure. 1 a) Single shot captures of masing signals at each hyperfine resonance for NV⁻ diamond. b) Diagram of the electromagnet and resonator with laser excitation, showcasing the small dimensions that can fit on the tabletop.

This lays the foundations for reducing the footprint of room temperature masers further, as well as spurs the search for new materials that could mase at different microwave frequencies, thus widening the applicable bandwidth of ultra-sensitive sensing which masers can provide. The immense reduction from 2000 kg electromagnets to a light 30 kg system opens opportunities for other research groups and industries to use the maser's exquisite low-noise capabilities in mobile communication and the growing quantum computing field, which relies on faint microwave signals for qubit readout.

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Variation of the nutation frequencies in scandium dimetallofullerenes

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Recently we have shown that the strong hyperfine interaction (HFI) of an ion reduces the effective magnetization [1]. The wave functions of the electron and nuclear spins coupled by the isotropic interaction are determined as

$$|\psi_{\pm,m}\rangle = \cos\sigma_{\pm}|\pm 1/2, m\rangle \pm \sin\sigma_{\pm}|\mp 1/2, m \pm 1\rangle.$$

Here the ket vectors are defined by projections of the electron ($\pm = \pm 1/2$) and nuclear (m) spins of the ion, respectively. This expression shows that the electron spin state is mixed and its projection along the quantization axis is reduced compared to the pure state. As a consequence, the interaction of the electron spin with the local environment is reduced. Thus, the strong contact Fermi interaction of an ion nucleus can affect the phase memory time as well as the frequency of the Rabi oscillation. The most significant reduction is expected for the ions with the large value of the nuclear spin I , when the nuclear spin projection is close to zero ($m = 0$ or $m = \pm 1/2$).

Nutation experiments on $\text{Sc}_2@\text{C}_{80}(\text{CH}_2\text{Ph})$ were used to study the Rabi frequency. This molecule exhibits unique properties due to nonlinear effects associated with the large HFI (509 MHz) and well-defined spin states [2]. Its EPR spectrum is fully resolved and has all 64 lines corresponding to the nuclear spin allowed transitions of two magnetically equivalent scandium ions $I(\text{Sc}) = 7/2$. Each EPR line can be assigned to the appropriate values of the total spin and the magnetic quantum number of the nuclei, j and m . This allows to examine the different spectral and relaxation properties depending on the spin state of the nuclei. Fig. 1 shows the variation of the transient nutation frequencies observed at 60K. The corresponding state of the nuclear spins, characterized by the values of j and m , is also indicated. Clearly, the frequency varies with the position of the EPR transition, decreasing gradually as the j value increases.

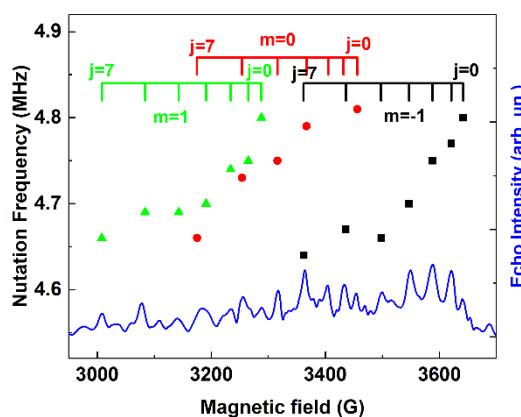


Figure 1. Dependence of the nutation frequencies on the EPR transition. Several m -values were examined: $m = 0$ (red), $m = -1$ (black), $m = 1$ (green). The echo-detected EPR spectrum is shown in blue.

The research was funded by RSF (project #22-43-04424). The scandium dimetallofullerene was provided by Dr. A. Popov, IFW Dresden, Germany.

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