Program and Abstracts

15th International Symposium
on
Spin and Magnetic Field Effects in Chemistry
and
Related Phenomena

September 17 – 21, 2017

Schluchsee (Black Forest), Germany

Sponsors

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Contents

Remembering Klaus Schulten

> ”When I was a young man, my goal was to look with mathematical and computational means at the inside of cells, one atom at a time, to decipher how living systems work. That is what I strived for and I never deflected from this goal.”
>
> Klaus Schulten (January 12, 1947 – October 31, 2016)

Klaus Schulten was a Professor of physics and Beckman Institute faculty member at the University of Illinois of Urbana-Champaign (USA) for nearly 25 years. He led the Theoretical and Computational Biophysics Group and was a key figure in modern computational biophysics, who devoted his life to unraveling the physical mechanisms underlying structural organization and function of supramolecular systems in the living cell, as well as to the development of non-equilibrium statistical-mechanical descriptions and efficient computing tools for structural biology. Klaus received his Ph.D. from Harvard University in 1974. At Illinois, he was Swanlund Professor of Physics and was affiliated with the Department of Chemistry as well as with the Center for Biophysics and Computational Biology; he was Director of the Biomedical Technology Research Center for Macromolecular Modeling and Bioinformatics as well as Co-Director of the Center for the Physics of Living Cells.

Klaus Schulten
(January 12, 1947 – October 31, 2016)

Klaus’s true passion for applying physical principles to complex biological problems has led to numerous pioneering discoveries that inspired several generations of scientists throughout the world. His research interest spanned across disciplines and involved application of quantum mechanics to magnetoreception and photosynthesis to studying atomistic dynamics of whole cells and cellular-scale structures.

The genius of Klaus’s mind made him predict biophysical phenomena before they were even revealed experimentally; the possible explanation of the magnetic compass sense in migratory birds is just one example. While working on magnetic-field effects on radical-pair reactions, Klaus proposed in 1978 a biomagnetic sensory mechanism based on magnetic-field-modulated coherent electron-spin motion. Based on this mechanism, in 2000 Klaus suggested that a radical-pair reaction in the then recently discovered blue-light photoreceptor protein cryptochrome could endow birds with magnetoreceptive abilities. The suggestion inspired numerous investigators, and cryptochrome is still considered the best candidate molecule for avian magnetoreception. A series of follow-up investigations established a firm ground for the hypotheses that the magnetic compass sense in birds involves the visual system and, in particular, the blue-light receptor cryptochrome.

Klaus was one of the leading scientists to advocate for the so-called "computational microscope", where mathematics, physics, chemistry and computing would act jointly to augment experimental research and lead to discoveries that would be impossible through experiments alone. The impact that Klaus left behind is not just measured through his 700+ published articles and over 100,000 citations, but also through the original thinking and approaches in solving complex problems.

This World has lost a great mind, a generous person, and a true friend. Klaus was an example to many students and scientists. He was a true inspiration and his passing is a huge loss for the scientific community.

Ilia A. Solov'yov

Welcome to the SCM 2017

On behalf of the International Spin Chemistry Committee as well as the Local Organizing Committee I would like to welcome you to Schluchsee, Black Forest, for the 15th International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena.

The “Spin Chemistry Meeting” (SCM), as it has come to be called for short, returns to Germany 25 years after the 2nd SCM took place in the city of Konstanz. It is hosted in a small Black Forest village, only about 75 km to the west of the site of the SCM 1992, however, in a completely different setting. I still vividly remember the Konstanz SCM, perfectly organized by Ulrich Steiner, as this was my first encounter with the Spin Chemistry Community, then as a young and eager Ph.D. student (of Gerd Kothe), new to the subject. I feel honored that now, a quarter of a century later, I have been entrusted by the International Spin Chemistry Committee led by Peter Hore, with the organization of the 15th meeting, now as a Professor of Physical Chemistry at the University of Freiburg.

It appears as if the right time was chosen for this meeting: more than 100 spin chemists from all over the world (United Kingdom, Japan, the United States of America, Russia, India, Switzerland, Canada, Denmark, China, Cyprus, Israel, Italy, The Netherlands, and Germany) are able to attend. The village of Schluchsee is located by the largest Black Forest lake at an altitude of nearly 1000 m above sea level. Beautiful forests and mountains, winding hiking paths and the fresh, clear air provide the perfect setting for a busy scientific program and numerous discussions centered around it. The town was also chosen because of its good train connection with Freiburg, which can be conveniently reached from the major airport hubs Frankfurt* and Zurich, or regional airports such as Basel/Mulhouse, Baden-Baden/Karlsruhe* and Stuttgart*.

I hope that you will enjoy the conference, the venue with its many amenities, the excursion to Freiburg (with a wine tasting session if you opted for it), and the banquet that will take place in a former traditional Black Forest farmhouse.

Last, but not least, I gratefully acknowledge tremendous support by the members of the International Spin Chemistry Committee and the Local Organizing Committee, Till Biskup, Jan-Bernd Hövener, Gerd Kothe and Christiane Timmel, in setting up this hopefully successful meeting.

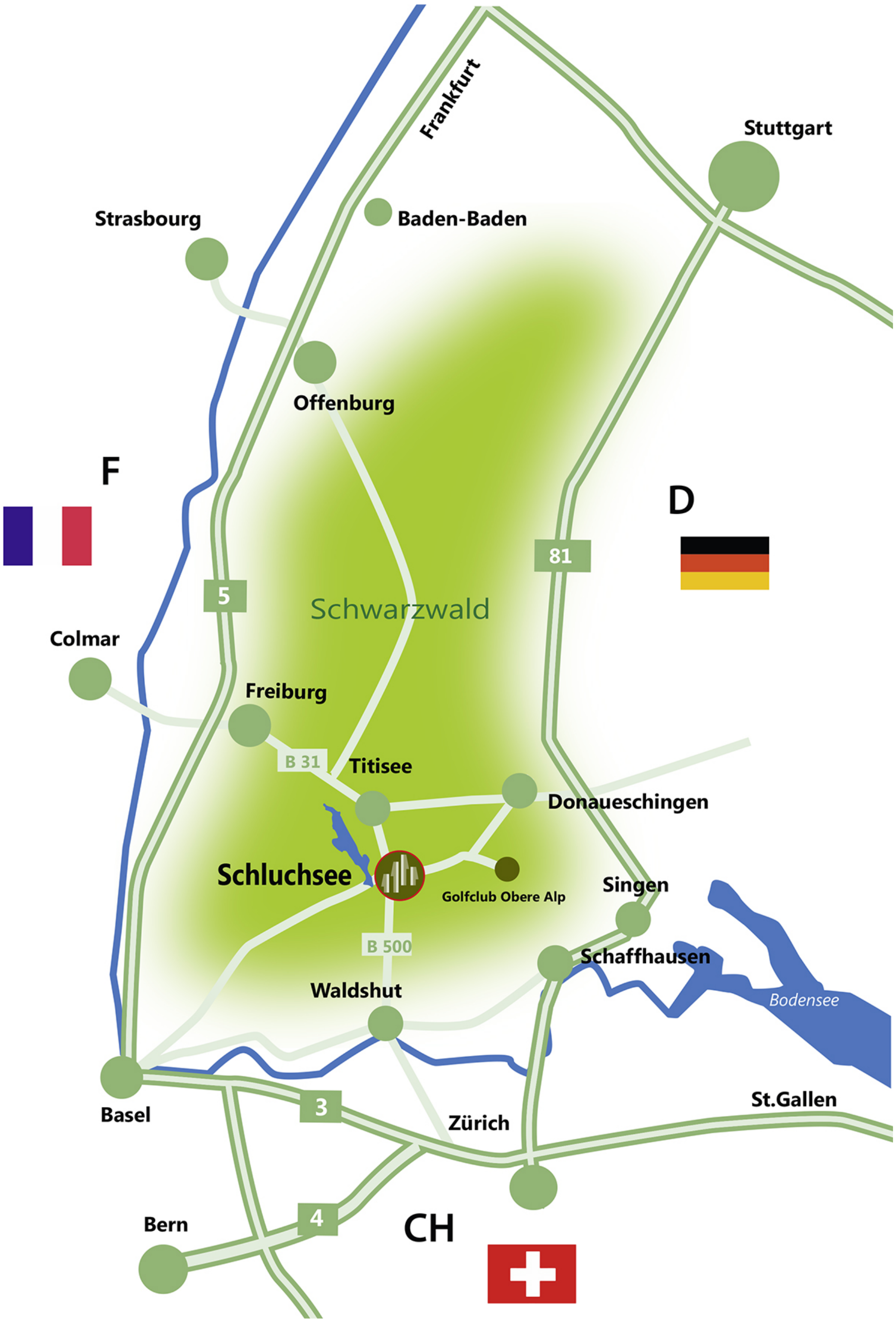
As they say here in the Black Forest to welcome visitors:

Salli!

Stefan Weber, Conference Chair
Spin Chemistry Meeting, 2017

*I could not foresee that German Rail (Deutsche Bahn) would unfortunately be forced to set up a train replacement service in one of the most important transport corridors in the wake of a major technical incident at a tunnel building site near Rastatt. Rail replacement means that those participants using this route have to change to a bus for part of their journey. I sincerely apologize for any inconvenience caused.

General Information



How to Get to Schluchsee

The town of Schluchsee can be easily accessed by **local trains** via Freiburg im Breisgau (Main Station, Platform 7).

Train	Departure Freiburg Hbf	Arrival Schluchsee
RB 17265	9:10	10:11
RB 17267	10:10	11:11
RB 17269	11:10	12:11
RB 17271	12:10	13:11
RB 17273	13:10	14:11
RB 17275	14:10	15:11
RB 17277	15:10	16:11
RB 17279	16:10	17:11
RB 17281	17:10	18:11
RB 17283	18:10	19:11
RB 17285	19:10	20:11
RB 17233	20:10*	21:22

*Change at Hinterzarten station to Bus 7255 (Departure at 20:55) that leaves just outside the train station.

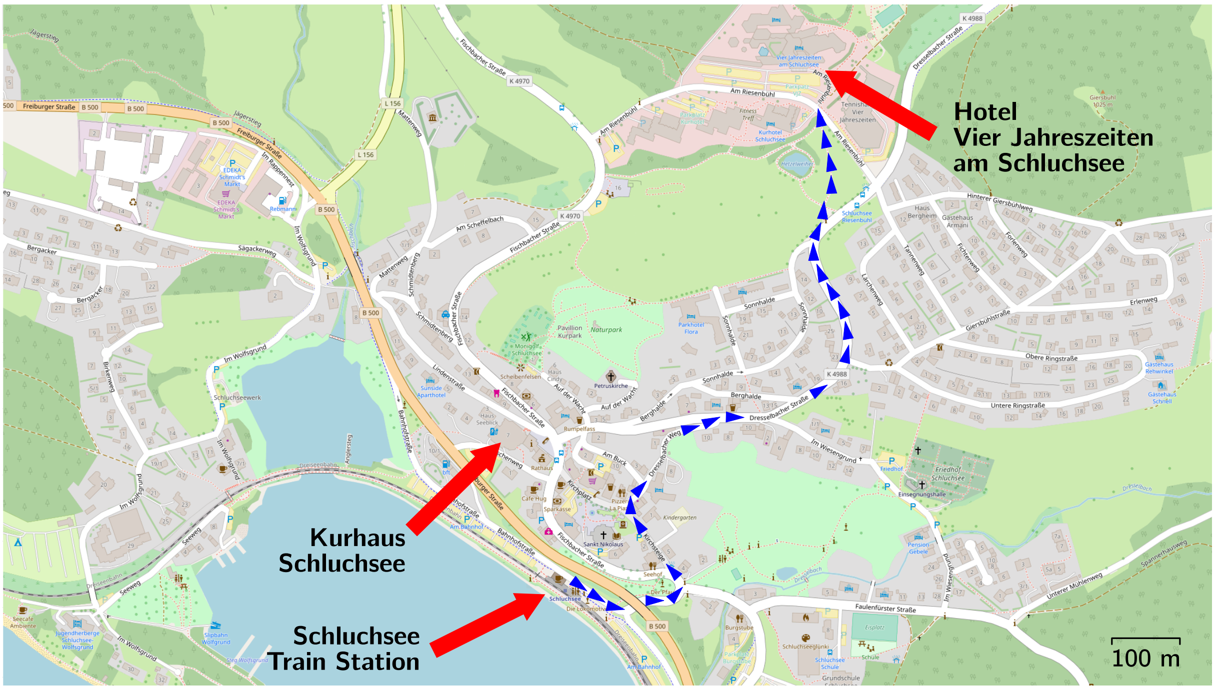
The railway line that connects Freiburg with Titisee is called “Höllentalbahn” (literally, “Hell Valley Railway”). It runs through the “Höllental” valley in the Black Forest. Over its entire course, the line rises from an altitude of 278 m in Freiburg to 885 m in Hinterzarten. Part of the route has a 5.5% gradient, making the line one of the steepest in Germany. The seats on the right-hand side (in the direction of travel) offer the nicer view of the scenery.

From Titisee on, the railway line is called “Dreiseenbahn” (literally, “Three Lakes Railway”) because it passes by the three lakes of “Titisee”, “Windgfällweiher” and “Schluchsee”. In the village of Schluchsee, the train reaches its final altitude of 932 m above sea level.

Conference Venue

The SCM 2017 will be held at the **Hotel “Vier Jahreszeiten am Schluchsee” (VJZ)**, 79859 Schluchsee (Black Forest, Germany), Am Riesenbühl 4 (GPS coordinates: 47°49’24.22” N / 8°10’54.11” E). The hotel is situated in the middle of the unique Southern Black Forest natural park at an altitude of about 970 m above sea level. Here you can find everything to take a break from everyday life and simply enjoy nature. It is an ideal place to feel great, take advantage of the extensive wellness and beauty area, and, foremost, to hear the latest news on spin and magnetic field effects in chemistry and related phenomena. Guests of the Hotel VJZ are welcome to use the 4,000-sqm indoor and outdoor swimming pool and spa area, sauna landscape and fitness studio for weights and endurance training. Bathrobes, flip-flops and a beach bag with a pool towel will be provided for the duration of your stay.

The Hotel VJZ is within walking distance from Schluchsee train station, see map (distance about 1.3 km; altitude difference 40 m; walking time about 15–20 min). Note, that free transfer from/to the train station is available for attendees with accommodation in the hotel. To order a shuttle bus, please call +49 (0)7656-700. There is parking available at the Hotel VJZ for those who would like to bring their own cars (5 € parking fee per day).



Registration/Conference Office

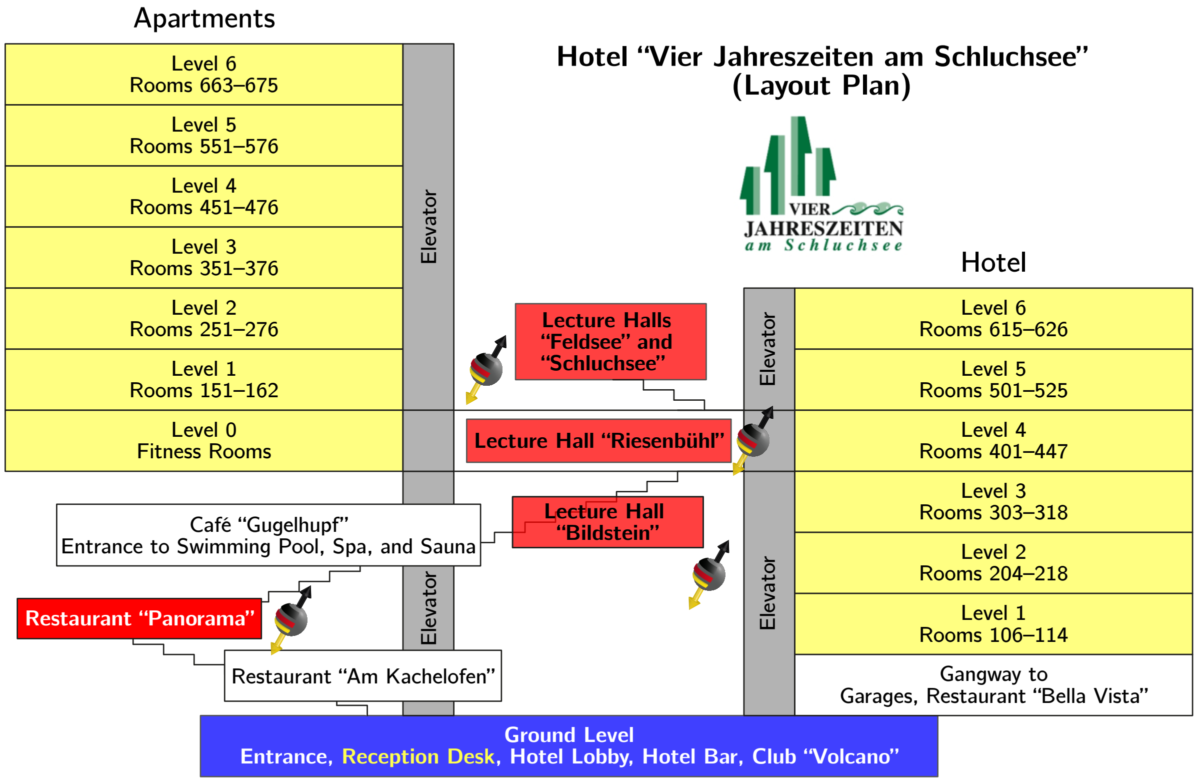
All conference attendees with accommodation in the Hotel "Vier Jahreszeiten am Schluchsee" should initially check in and collect the keys to their rooms from the hotel reception, which is open permanently 24 hours a day for check in. The rooms and apartments are available on the day of arrival from 15:00 and must be vacated by 11:00 on the day of departure.

The **conference office** will be open on Sunday (September 17) from 15:00 to 18:30 for registration to the conference for all attendees. The office will be signposted from the hotel reception. On all other days, conference registration will be open between 9:00 and 12:00, and during the coffee breaks.

Lectures

The **opening lectures** on Sunday (September 17) will be held after the Welcome Reception in the **Kurhaus Schluchsee**, 79859 Schluchsee (Black Forest, Germany), Fischbacher Str. 7 (GPS coordinates: 47°49'07.91" N / 8°10'35.68" E), see map below.

All other lectures, from Monday (September 18) to Thursday (September 21), will be held in the **"Riesenbühl" lecture hall** of the **Hotel VJZ**, see schematic drawing of the hotel layout.



Information for Speakers

Excluding discussion time, **keynote lectures** will be **35 minutes**, **invited lectures 25 minutes**, and **contributed lectures 20 minutes**. Please allow 5 minutes for discussion after invited and contributed lectures, and 10 minutes after a keynote lecture. All speakers are kindly asked to coordinate the contents of their lecture and to avoid repetitive introductions: the keynote lecturers were asked to review their respective field of research before presenting own data.

A data projector and a conference laptop will be available. Speakers are kindly asked to upload their presentations onto this computer (ideally as a PDF file or a Microsoft PowerPoint file) and set up and test them well before their presentation. If it is strictly necessary, speakers may use their own laptops (please provide necessary adapters to connect to the projector, especially when you use Apple computers), but we discourage this in order to minimize the switch-over time between presentations. Members of the local organizing team will be available to open the lecture theatre and provide limited technical assistance.

Please would all speakers ensure they keep strictly to the time schedule.

Posters

Poster sessions will take place on **Tuesday** and **Wednesday** in the **“Feldsee” and “Schluchsee” lecture rooms**. These rooms will be signposted from the “Riesenbühl” lecture hall. Poster size will be A0, *i.e.*, 1189 mm (height) × 841 mm (width).

Posters should be set up either on Monday or Tuesday in the morning and removed on Thursday morning. Posters are identified by their numbers given in this booklet. Please affix your poster to the corresponding numbered board only, using the pins provided.

The authors are requested to be at their posters during their scheduled poster sessions:

- Poster Session 1, **Tuesday** (September 19) from 20:30 – 22:00: **odd** numbers;
- Poster Session 2, **Wednesday** (September 20) from 20:30 – 22:00: **even** numbers.

There will be a "Taylor & Francis" **Poster Prize** for the best three posters.

WiFi

Wireless internet will be available in all bedrooms of the Hotel "Vier Jahreszeiten am Schluchsee" and the "Riesenbühl" lecture hall. Details on how to connect to the internet will be provided during registration.

Coffee Breaks

Coffee, tea, and water will be provided during the coffee breaks that take place in the **"Bildstein"** lecture hall.

Lunch and Dinner

For attendees with accommodation in the Hotel "Vier Jahreszeiten am Schluchsee", breakfast (buffet style) will be served from 7:00 to 10:30 in the Restaurant "Panorama".

With the exception of the Welcome Reception on Sunday evening in the "Kurhaus Schluchsee" and the Conference Banquet on Thursday evening in the "Waldhotel Fehrenbach" (Hinterzarten), all lunches and dinners provided during the conference will be served in the Restaurant "Panorama". The exact times for lunches and dinners vary slightly from day to day depending on the scientific program. On Thursday (September 21), lunch boxes will be provided for the excursion to Freiburg. Please note, that **lunches and dinners**, as well as the buffet at the Welcome Reception and the Conference Banquet **are included in the registration fees** of regular and Ph.D. student participants, and participants from industry. This also holds for a selection of non-alcoholic beverages (excluding non-alcoholic beer) served during regular lunches and dinners.

Conference Banquet

The Conference Banquet will take place on Thursday (September 21), from 19:30 to 22:00, in the **"Waldhotel Fehrenbach"**, 79856 **Hinterzarten**, Alpersbach 9 (GPS coordinates: 47°54'31.96" N / 8°03'11.67" E). Busses will bring all conference attendants after the Freiburg excursion to the Waldhotel. Conference participants that do not join the excursion are kindly requested to organize their own journey to the Conference Banquet site. After the Conference Banquet, busses will bring all attendants back to Schluchsee (arrival at about 22:30).

Accompanying Persons

Although there is no additional formal program of events for accompanying persons, the conference organizers will be happy to suggest interesting places to visit within the Schluchsee area, Freiburg, and beyond. Please contact Mrs. Sigi Kothe (sigi.kothe@t-online.de) for further information. Here come some suggestions for activities, that can be organized on request:

- **Titisee (lake and town)** (GPS coordinates: 47°53'58.05" N / 8°09'09.04" E):
  The "Titisee" is the largest natural lake in the Black Forest. It stretches for some 2 km. It is a popular resort destination, with plenty of outdoor activities.
  Follow the 5-mile/8-km trail around the lake: On the east side, the trail follows the water; on the west side, it goes up the Hochfirst Mountain, giving splendid views over the valley.
  Or get out on to the water: take a cruise on the lake, go windsurfing or sailing, or just rent a rowing boat and do your own thing. Then relax in a typical beer garden in the town of Titisee.
  (Distance from Schluchsee by train: about 22 km)
- **Feldberg Mountain** (http://www.feldbergbahn.de) (GPS coordinates: 47°51'38.00" N / 8°02'05.96" E):
  At 1,493 m, the "Feldberg" is the highest mountain in the Black Forest and in Baden-Württemberg, and the highest in Germany outside the Alps. Enjoy idyllic trails and magnificent panoramas on and around the Feldberg.
  (Feldbergbahn: €9,50 per person; reduced fees for children; Distance from Schluchsee: about 17 km by car)
- **Hasenhorn Coaster in Todtnau** (http://www.hasenhorn-rodelbahn.de) (GPS coordinates: 47°49'44.06" N / 7°56'53.61" E):
  This is the most spectacular and longest (2.9 km) toboggan coaster in Germany.
  (One ride: €9,50 per person; reduced fees for children; Distance from Schluchsee: about 27 km by car)
- **Schwarzwälder Freilichtmuseum Vogtsbauernhof** (http://en.vogtsbauernhof.de) in Gutach (GPS coordinates: 48°16'16.60" N / 8°11'54.62" E):
  The museum is centered on the "Vogtsbauernhof" farmhouse dating from 1612, which was built on this site. Other historic buildings from other parts of the Black Forest have been dismantled, transported to the museum and reassembled. Six fully furnished farmhouses, the

day labourer's cottage and 15 outbuildings, such as mills, sawmills, barns, stalls, a chapel, storehouses and a granny house (Leibgedinghaus), invite you to take a stroll and discover the multifaceted aspects of the historic Black Forest way of life.
(Entrance fee: €9,00 per person; reduced fee for children; Distance from Schluchsee: about 95 km by car)

- Further suggestions can be found at

  https://www.hochschwarzwald.de

  http://www.blackforest-tourism.com

Registered accompanying persons are invited to join the Welcome Reception on Sunday, the excursion to Freiburg, and the Conference Banquet on Thursday evening.

Scientific Program

Sunday, September 17, 2017

Kurhaus Schluchsee (79859 Schluchsee, Fischbacher Str. 7)
(GPS coordinates: 47°49’07.91” N / 8°10’35.68” E)

19:00 – 20:25	**Welcome Reception**
20:25 – 20:30	**Stefan Weber** Welcome Note
	Chair: Stefan Weber
20:30 – 21:15	(T1) **Peter J. Hore** Spin chemistry and related phenomena

Monday, September 18, 2017

Hotel ”Vier Jahreszeiten am Schluchsee” (79859 Schluchsee, Am Riesenbühl 4)
(GPS coordinates: 47°49’24.22” N / 8°10’54.11” E)

”Riesenbühl” lecture hall

Chair: Michael R. Wasielewski

9:00 – 9:45 (T2) **Takeji Takui**
Molecular spin-based quantum information science and technology.
Molecular spin qubits and quantum control

9:45 – 10:15 (T3) **Ron Naaman**
Electron spin and chirality. From molecular spintronics to enantio recognition

10:15 – 10:40 (T4) **Martin T. Lemaire**
Polynuclear transition metal-aminyl free radical complexes

10:40 – 11:15 Coffee break (”Bildstein” lecture hall)

Chair: Robert Bittl

11:15 – 11:45 (T5) **Marilena Di Valentin**
Triplet-state spin labels for high-sensitive PELDOR spectroscopy

11:45 – 12:10 (T6) **Christopher W.M. Kay**
Nanosecond time-resolved characterization of a pentacene-based
room-temperature MASER

12:10 – 12:35 (T7) **Sabine Richert**
Exploring the factors governing the extent of triplet-state delocalization
in linear porphyrin oligomers

12:40 – 14:00 Lunch (Restaurant ”Panorama”)

Chair: Peter J. Hore

14:00 – 14:45 (T8) **Spiros S. Skourtis**
Electron transfer processes from the molecular to the cellular length scales

14:45 – 15:15 (T9) **David A. Shultz**
Wavefunction control of charge-separated excited-state spin polarization
and lifetimes

15:15 – 15:40 (T10) **Thomas P. Fay**
Spin-dependent mechanisms of charge transport along oligophenylene
molecular wires

15:40 – 16:15 Coffee break (”Bildstein” lecture hall)

Chair: Till Biskup

16:15 – 17:00 (T12) **Tadaaki Ikoma**
Magnetic field effect on carrier dynamics in organic solar cells

17:00 – 17:30 (T13) **Jan Behrends**
Spin-dependent processes in organic solar cell materials

17:30 – 17:55 (T14) **Leonid Kulik**
Structure and spin-dependent recombination of charge-transfer states
in photovoltaic polymer/fullerene composites

17:55 – 18:20 (T15) **Andreas Sperlich**
Triplet exciton loss channels in organic solar cells

18:20 – 20:00 Dinner (Restaurant ”Panorama”)

Chair: James R. Norris

20:00 – 20:25 (T16) **Malcolm D.E. Forbes**
Not so free radicals

20:25 – 20:50 (T17) **Hisao Murai**
Considerations to CIDEP of photolyzed inclusion compounds

20:50 – 21:15 (T18) **Tomoaki Miura**
Gigantic magnetic field effect on long-lived charge separated states
created at a nonionic vesicle interface

21:15 – 21:40 (T19) **Laura C. Motta**
Magnetic isotope effect in the environment.
A study of mercury stable-isotope fractionation

Tuesday, September 19, 2017

Hotel ”Vier Jahreszeiten am Schluchsee” (79859 Schluchsee, Am Riesenbühl 4)
(GPS coordinates: 47°49’24.22” N / 8°10’54.11” E)

”Riesenbühl” lecture hall

Chair: Kiminori Maeda

9:00 – 9:55 (T20) **Christiane R. Timmel** & (T21) **Erik Schleicher**
Millitesla magnetic field effects on the photocycle of an animal cryptochrome
Paramagnetic intermediate states in cryptochromes

9:55 – 10:25 **Robert Bittl & Ilia Solov’yov**
The radical-pair model and animal magnetoreception: how it all began.
In memoriam Klaus Schulten

10:25 – 10:50 (T22) **Weidong Pan**
Behavioral evidence for the orientation of rice planthopper *Nilaparvata lugens* using a magnetic cue

10:50 – 11:20 Coffee break (”Bildstein” lecture hall)

Chair: Christiane R. Timmel

11:20 – 11:45 (T23) **Ilia Solov’yov**
Molecular insights into electron transfers in cryptochrome

11:45 – 12:10 (T24) **Daniel R. Kattnig**
Radical-pair based magnetoreception amplified by radical scavenging

12:10 – 12:35 (T25) **Susannah Worster**
Testing the cryptochrome hypothesis of magnetoreception:
a ‘killer’ experiment?

12:35 – 14:00 Lunch (Restaurant ”Panorama”)

Chair: Gerd Kothe

14:00 – 14:25 (T26) **Kiminori Maeda**
Radical pair spin lifetime and dynamics studied by static and pulsed magnetic field

14:25 – 14:50 (T27) **Samita Basu**
Magnetic field effect. An assessor of donor–acceptor separation
in photoinduced reaction

14:50 – 15:15 (T28) **Christian Kerpal**
Magnetic field effect anisotropy. A chemical compass in the low field region

15:15 – 15:40 (T29) **Lauren E. Jarocha**
Engineering an artificial flavoprotein as a model for radical pair-based magnetosensors

15:40 – 16:05 (T30) **Jonathan R. Woodward**
Microspectroscopic studies of flavin-based radical pairs

16:05 – 16:45 Coffee break (”Bildstein” lecture hall)

Chair: Konstantin N. Ivanov

16:45 – 17:30 (T31) **Silvia Cavagnero**
New avenues in photochemically induced dynamic nuclear polarization in liquids

17:30 – 17:55 (T32) **Jörg Matysik**
The solid-state photo-CIDNP effect

17:55 – 18:20 (T33) **Christopher J. Wedge**
Exploiting radical–triplet pair hyperpolarization for sensitivity enhancement
in solution-state NMR

18:20 – 18:45 (T34) **Alexandra V. Yurkovskaya**
Competition of singlet and triplet recombination of radical pairs in photoreactions
of 3,3′,4,4′-tetracarboxy benzophenone with biologically important molecules

18:45 – 19:10 (T35) **Lokesh Nanjundappa**
NMR detection and characterization of transient reaction intermediates

19:15 – 20:30 Dinner (Restaurant ”Panorama”)

20:30 – 22:00 **Poster Session** (odd numbers) (**”Feldsee” and ”Schluchsee” lecture halls**)

Wednesday, September 20, 2017

Hotel "Vier Jahreszeiten am Schluchsee" (79859 Schluchsee, Am Riesenbühl 4)
(GPS coordinates: 47°49'24.22" N / 8°10'54.11" E)

"Riesenbühl" lecture hall

Chair: Jürgen Hennig

9:00 – 9:45	(T36) **Simon Duckett** Harnessing parahydrogen as a source of hyperpolarization
9:45 – 10:15	(T37) **Warren S. Warren** Next-generation coherent methods for efficient molecular hyperpolarization
10:15 – 10:40	(T38) **Thomas Theis** Hyperpolarization chemistry for applications ranging from chemical analysis to affordable molecular imaging
10:40 – 11:15	Coffee break ("Bildstein" lecture hall)

Chair: Jan-Bernd Hövener

11:15 – 11:45	(T39) **Gerd Buntkowsky** Ultra-sensitive detection of catalytic intermediates. The PANEL experiment
11:45 – 12:15	(T40) **Stefan Glöggler** Parahydrogen induced polarization. Nanocatalysts and metabolites
12:15 – 12:35	(T11) **Sylwia Kacprzak** Solutions for high-end research to routine analytical tasks
12:35 – 14:00	Lunch (Restaurant "Panorama")

Chair: Tadaaki Ikoma

14:00 – 14:45	(T42) **Christopher J. Bardeen** Spin state dynamics in exciton fission and fusion
14:45 – 15:10	(T43) **Tomoaki Yago** Characterization of triplet pairs generated by singlet fission
15:10 – 15:35	(T44) **Michael R. Wasielewski** Zero quantum coherence in covalent spin-correlated radical pairs
15:35 – 16:00	(T45) **Vsevolod Borovkov** Recombination fluorescence as a way of probing the spin-correlated radical ion pairs created in polymeric systems by high-energy radiation

16:00 – 16:30	Coffee break (”Bildstein” lecture hall)
	Chair: Leonid Kulik
16:30 – 17:15	(T46) **John M. Lupton** Magnetic field effects in organic semiconductors
17:15 – 17:40	(T47) **Yoshio Teki** Photoconductivity and magnetoconductance effect on vacuum vapor deposition films of weak charge-transfer complexes
17:40 – 18:05	(T48) **Nikita N. Lukzen** Conversion of singlet spin state of pair of radicals coupled with exchange or dipole-dipole interaction into non-zero total spin hyperpolarization by means of adiabatic switching of strong microwave field
18:05 – 18:30	(T49) **Christoph Lambert** Charge separation and recombination in triads based on dipyrrin complexes of iridium, palladium and platinum
18:30 – 18:55	(T50) **Ulrich E. Steiner** Global energy functions for spin processes in radical pairs
18:55 – 20:30	Dinner (Restaurant ”Panorama”)
20:30 – 22:00	**Poster Session** (even numbers) (**”Feldsee” and ”Schluchsee” lecture halls**)

Thursday, September 21, 2017

Hotel "Vier Jahreszeiten am Schluchsee" (79859 Schluchsee, Am Riesenbühl 4)
(GPS coordinates: 47°49'24.22" N / 8°10'54.11" E)

"Riesenbühl" lecture hall

Chair: Gerd Buntkowsky

9:00 – 9:45	(T51) **Konstantin L. Ivanov** The role of level anti-crossings in nuclear spin hyperpolarization
9:45 – 10:10	(T52) **Hans-Martin Vieth** Effects of very low magnetic fields on nuclear hyperpolarization
10:10 – 10:35	(T53) **Denis V. Sosnovsky** Level anti-crossing concept and analysis of CIDNP and ONP in solids
10:35 – 10:50	Coffee break ("Bildstein" lecture hall)

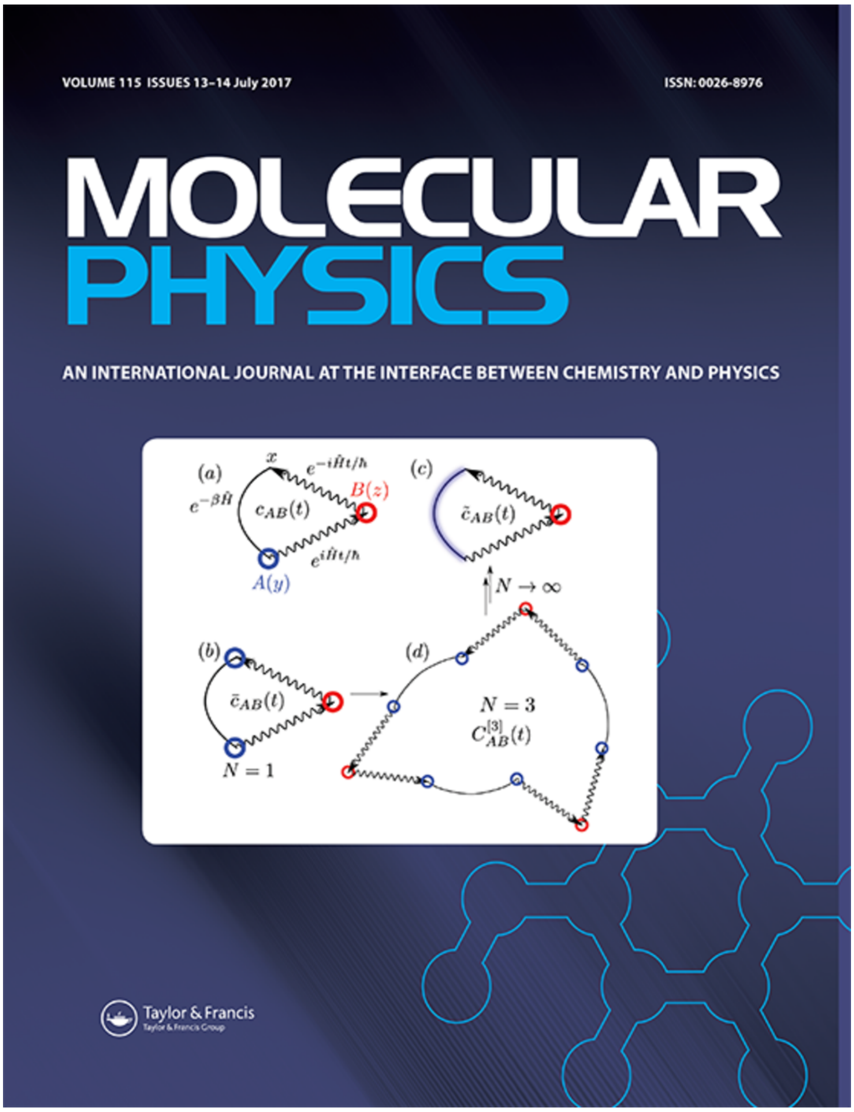
Chair: Malcolm D.E. Forbes

10:50 – 11:35	(T54) **Art van der Est** Electron spin polarization in natural and artificial photosynthesis
11:35 – 12:00	(T55) **Yasuhiro Kobori** Electron spin polarization imaging of photoinduced primary charge-separated states in PSII

12:45 – 18:30	**Excursion to Freiburg**
19:30 – 22:00	**Conference Banquet** ("Waldhotel Fehrenbach", Hinterzarten)
about 22:30	Return at the Hotel "Vier Jahreszeiten am Schluchsee"

Call for Contributions to Special Issue

A special issue of "Molecular Physics" will be devoted to contributions (both lectures and posters) presented at the SCM 2017. This issue will be edited by Christiane R. Timmel (Oxford, United Kingdom), Art van der Est (St. Catharines, Canada) and Stefan Weber (Freiburg, Germany). We aim at **January 31, 2018** as **submission deadline**. Generally it takes around six months for reviewing, revisions and putting the manuscripts into production, so we plan to publish in fall 2018.



The International Spin Chemistry Committee

Samita Basu (Kolkata, India)

Art van der Est (St. Catharines, Canada)

Malcolm Forbes (Bowling Green, USA)

Günter Grampp (Graz, Austria)

Peter Hore, Chairman (Oxford, United Kingdom)

Konstantin Ivanov (Novosibirsk, Russia)

Yasuhiro Kobori (Kobe, Japan)

Leonid Kulik (Novosibirsk, Russia)

Jörg Matysik (Leipzig, Germany)

Kiminori Maeda (Saitama, Japan)

Michael Wasielewski (Evanston, USA)

Stefan Weber (Freiburg, Germany)

Markus Wohlgenannt (Iowa City, USA)

For more information on the activities of the International Spin Chemistry Community, please check out the corresponding website:

`http://www.spinchemistry.org/`

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Abstracts of Talks

Spin chemistry and related phenomena

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When, in 1976, the distinguished Oxford chemist Peter W. Atkins (later even more famous as the author of the world's best-selling Physical Chemistry textbooks) wrote that "*the study of the effect of magnetic fields on chemical reactions has long been a romping ground for charlatans*" [1], he was not referring to Spin Chemistry, a subject then in its infancy. Having swiftly dismissed "*contributions to the literature of the subject* [that] *range over the span of scientific competence, from the benignly insane to whatever lies at the other extreme removed by a hair's breadth from the first*", he went on to review "*a body of modern literature which seems reliable*", namely the early experimental and theoretical work on the effects of magnetic fields on the reactions of radicals and triplet states which, together with even earlier studies of chemically induced spin polarization, formed the basis of the now mature field of Spin Chemistry. Atkins went on to mention, and swiftly dispose of, the "*facile thermodynamic argument*" against the existence of chemical magnetic field effects: that the interactions of molecules with even the strongest available magnetic fields are tiny in comparison with $k_\mathrm{B}T$ (the thermal energy, Boltzmann's constant × temperature).

In this overview lecture I will attempt to summarize the remarkable properties of radical pairs and related species that make them extraordinarily sensitive to magnetic interactions that are orders of magnitude smaller than $k_\mathrm{B}T$ – not just the interactions of electron spins and nuclear spins with applied magnetic fields but also the interactions of spins with one another.

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Molecular spin-based quantum information science and technology. Molecular spin qubits and quantum control

Kazunobu Sato[1], Satoru Yamamoto[1], Taiki Shibata[1], Elham Hosseini[1], Kenji Sugisaki[1], Shigeaki Nakazawa[1], Koji Maruyama[1], Kazuo Toyota[1], Daisuke Shiomi[1], Shuichi Suzuki[1,‡], Keiji Okada[1] and Takeji Takui[1,2]

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Quantum computing and quantum information processing (QC/QIP) have emerged in advanced fields including spin science/chemistry. In contrast to existing advanced molecular detection technology, quantum cybernetics approaches relevant to quantum control feature in molecular spin-qubit science and technology.

In the field of QC/QIP, single-molecule/photon-manipulation techniques seem essential in illustrating the physical realization of qubits, but an ensemble approach has some advantages over current single-particle manipulation technology. Both the single-particle and ensemble approaches are useful to implement QC/QIP technology. In recent development of QC/QIP, all the relevant physical qubits are facing the problem of the scalability of relevant qubits in addition to decoherence intrinsic to their quantum nature. Among candidates for physically realized qubits, molecular spin qubits are the latest arrival [1–3], but have their own right [4,5].

We introduce the latest achievements based on molecular spin qubits in ensembles, discussing their advantages and disadvantages in terms of quantum spin technology [3,6]. Attempts to apply molecular spins to the implementation of QC/QIP have been underlain by enormous efforts by organic chemists to synthesize stable molecular spins, which fulfill the requirements of spin qubits for QC gate operations. In terms of the gate operations, we utilize weakly exchange-coupled multi-partite electron-spin systems because of the limitations of current pulse microwave technology, which enables us to manipulate or control matter spin qubits. In order to implement practical QC/QIP systems, a large number of quantum memory elements are required as well. We illustrate that open-shell chemistry plays an important role to afford the memory elements for the architecture of scalable superconducting flux qubits or microwave photons.

Molecular spin qubits, properly designed, can also give a testing ground for "Adiabatic Quantum Computing", which is different from the standard circuit model of quantum computing, and thus, an alternative approach to QC/QIP. From the theoretical point of view, among theoretical attempts, the implementation of practical quantum algorithms for quantum chemistry is essential in QC/QIP [7].

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Electron spin and chirality. From molecular spintronics to enantio recognition

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In the last decade it was found that chiral organic molecules act as spin filters for photoelectron transmission [1], in electron transfer [2], and in electron transport [3]. The new effect, termed "Chiral Induced Spin Selectivity" (CISS) [4,5], was found, among others, in biomolecules and in biosystems. It has interesting implications for the production of new types of spintronics devices [6,7], and on electron transfer in biological systems [8]. The effect will be described and its implications for spintronics and enantio-recognition processes will be presented.

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Polynuclear transition metal-aminyl free radical complexes

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Redox-active ligands (RALs) that can be readily oxidized or reduced to produce stable, open-shell species, are an ideal scaffold for the creation of molecule-based magnetic materials that may find application in the burgeoning field of molecular spintronics. The coordination of RALs to transition metal or lanthanide ions has become a successful strategy toward the preparation of paramagnetic switching materials [1], single molecule magnets (SMMs) [2], and recently, electrically conducting metal-organic frameworks (MOFs) [3]. Open-shell ligands have been shown to mediate strong magnetic exchange coupling with metal ions, resulting in well-isolated high-spin ground states and better SMM behavior. When open-shell ligands are incorporated into paramagnetic switching materials (spin-crossover complexes or valence tautomers), the potential for new multifunctional behaviours is great (spin-crossover conductors, for example [4]).

We are interested in the development and study of new polytopic RALs to produce strong magnetic coupling in polynuclear cluster complexes as well as to generate novel types of switching materials. In this regard, we have recently developed a synthetic strategy to produce ditopic RALs with the structure outlined in Figure 1 [5]. Somewhat surprisingly, we have isolated a stable phenoxyl radical (Figure 1, right) by oxidation of the fully reduced "phenol" precursor (Figure 1, left). These phenoxyl radicals feature intense NIR absorptions ($\approx$ 1150 nm), air/moisture stability, and in some instances solution based magnetic switching properties. Coordination of the phenol precursor produces polynuclear complexes of the form M_4L_4 or $[M_5L_4]_2ClO_4$ (M = Fe, Co, Cu, Zn), in which the ligand (L) is in a completely different open-shell form (dianion aminyl radical). In this presentation we will highlight the structure and properties of these complexes and discuss current efforts to synthesize larger ligands and complexes.

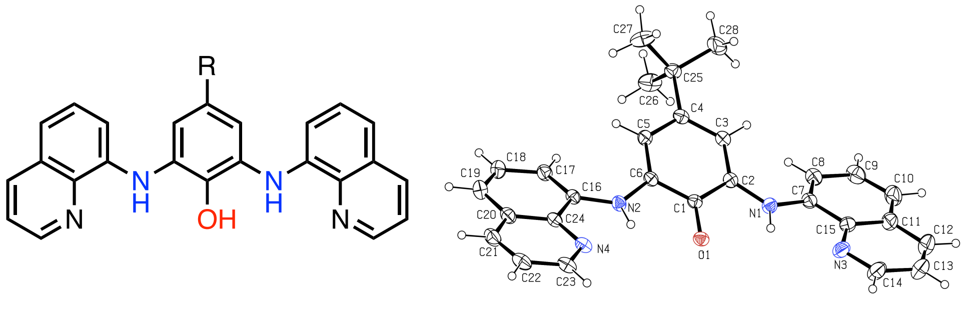

Figure 1: Phenolic precursor (left) and structure of stable ditopic phenoxyl radical (right). R = *t*Bu, Me, NO_2, NH_2.

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Triplet-state spin labels for high-sensitive PELDOR spectroscopy

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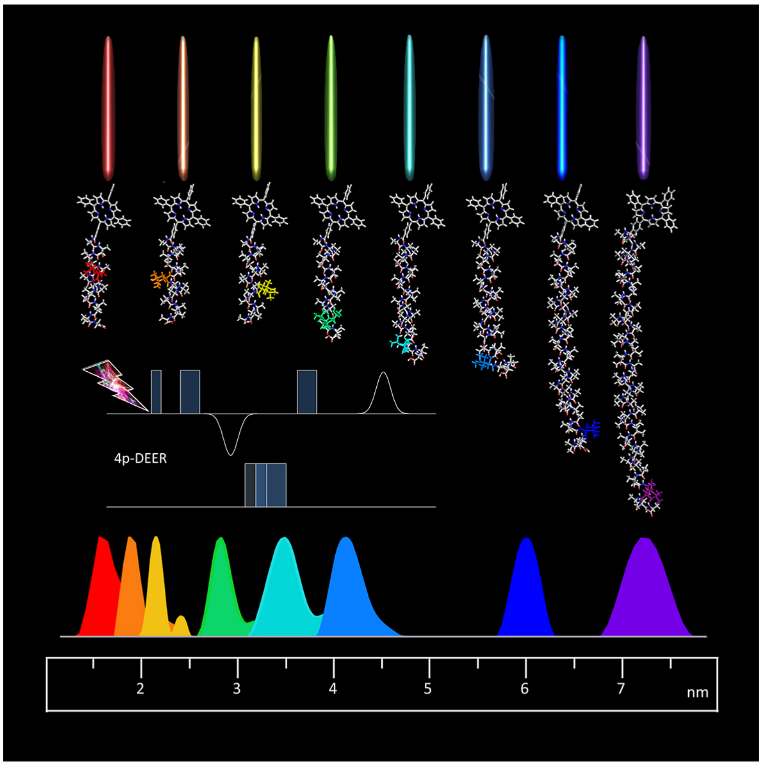
We present a novel pulsed electron paramagnetic resonance spectroscopic ruler to test the performance of a recently developed spin-labelling method for measuring on a nanometer scale based on the photoexcited triplet state [1]. Four-pulse electron double resonance (PELDOR) experiments were carried out on a series of helical peptides, labeled at the N-terminal end with the porphyrin moiety, which can be excited to the triplet state, and with the nitroxide at various sequence positions, spanning distances in the range from 18 to 80 Å. The PELDOR traces provide accurate distance measurements for all the ruler series, showing deep envelope modulations at frequencies varying in a progressive way according to the increasing distance between the spin labels. The upper distance limit is evaluated and found to be around 80 Å. The PELDOR-derived distances are in excellent agreement with theoretical predictions. We demonstrate that high sensitivity is acquired using the triplet state as spin label by comparison with Cu(II) porphyrin analogs. This is due to spin polarization acquired by selective intersystem crossing.

The methodology has been extended from the peptide model system to paradigmatic proteins, where the triplet-state spin probe is endogenous, proving that this labelling approach has a high potential for measuring nanometer distances in more complex biological systems [2].



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Nanosecond time-resolved characterization of a pentacene-based room-temperature MASER

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The performance of a room-temperature, zero-field MASER operating at 1.45 GHz has been examined [1]. Nanosecond laser pulses, which are essentially instantaneous on the timescale of the spin dynamics, allow the visible-to-microwave conversion efficiency and temporal response of the MASER to be measured as a function of excitation energy. It is observed that the timing and amplitude of the MASER output pulse are correlated with the laser excitation energy: at higher laser energy, the microwave pulses have larger amplitude and appear after shorter delay than those recorded at lower laser energy.

The dynamics of the MASER emission may be modelled by a pair of first-order, non-linear differential equations, derived from the Lotka-Volterra model (Predator-Prey), whereby the microwave mode of the resonator is the predator and the spin polarization in the triplet state of pentacene is the prey. Simulations allowed the Einstein coefficient of stimulated emission, the spin-lattice relaxation and the number of triplets contributing to the MASER emission to be estimated. These are essential parameters for the rational improvement of a MASER based on a spin-polarized triplet molecule.

In a second set of experiments with a crystal containing a higher concentration of pentacene, we observe Rabi oscillations in the MASER output [2]. Fourier transformation of the time-domain spectrum reveals a splitting proportional to the square root of the number of spins, which indicates strong coupling between the collective spin ensemble and the microwave photons. Furthermore, we also observe a cavity protection effect, which decreases the polariton decay rate as the collective coupling increases. Access to the strong-coupling regime is essential for efficient transfer of excitations between states in different quantum systems on timescales shorter than their lifetimes. Thus, our discovery paves the way for room-temperature quantum information processing devices such as spin memories and quantum-enhanced technologies for metrology, sensing, communications and ultimately, quantum computing.

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Exploring the factors governing the extent of triplet-state delocalization in linear porphyrin oligomers

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Photoexcited triplet states play an important role in many photochemical mechanisms. Long known to be of paramount importance in the study of photosynthetic reaction centers, they have more recently also been shown to play a major role in a number of applications in the field of molecular electronics. Their characterization is crucial for an improved understanding of the underlying processes with a particular focus on the determination of the spatial distribution of the triplet-state wavefunction, providing information on charge and energy-transfer efficiencies [1,2]. Currently, active research in this field is mostly focussed on the investigation of materials for organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs) [3].

Since the properties of triplet states and their spatial extent are known to have a major impact on device performance, a detailed understanding of the factors governing triplet-state delocalization is at the basis of the further development and improvement of these devices. In this contribution, we investigate triplet-state delocalization in a range of linear zinc-porphyrin oligomers (cf. Figure 1) by transient continuous-wave and pulse electron paramagnetic resonance spectroscopy and discuss the factors governing the spatial extent of the triplet wavefunction [4,5].

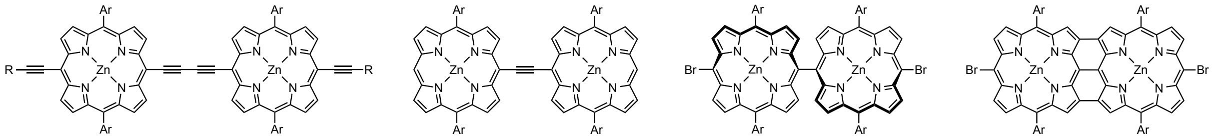

Figure 1: Selected examples of the investigated structures.

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Electron transfer processes from the molecular to the cellular length scales

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Molecular electron transfer reactions are ubiquitous in chemistry and biology [1]. In biology, biomolecular electron transfer chains are involved in signaling, in the creation and control of disease and are essential components of bioenergetic processes operating from the single-molecule to the cellular levels. A grand project in the field is to understand the roles of biomolecular structure and dynamics on electron transfer mechanisms and to connect the single molecule (quantum mechanical) to the cellular (kinetic network) length scales [2]. I give a review of the current status of the electron transfer field and I discuss open questions and future challenges.

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Wavefunction control of charge-separated excited-state spin polarization and lifetimes

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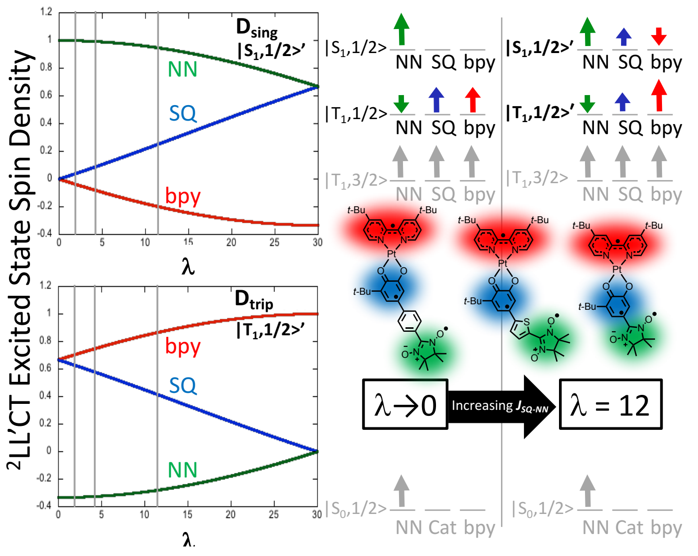
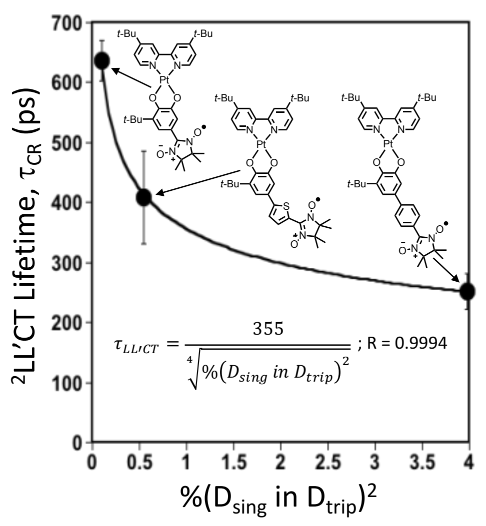
Entangled states form a basis for quantum computing and quantum information technologies. Preparation and control of entangled spin states allows for the manipulation of polarization effects involving nuclear and electron spin populations, thus providing a spin-based mechanism for high density storage of information in quantum states. This presentation will describe an excited state mechanism for precise control of quantum-entangled states based on a series of donor-acceptor (D-A) dyads possessing a covalently-attached stable radical. This mechanism derives from excited state magnetic exchange couplings that occur between the electron spin of the radical, and those of a photo-generated electron-hole pair. The entanglement is initiated by ultrafast absorption of a photon and modified by subsequent relaxation within the excited-state spin manifolds, leading to dramatic changes in spin polarization between excited states of the same multiplicity. The photo-initiated entanglement can be "read" via magnetic circular dichroism (MCD) spectroscopy, a technique that is sensitive to excited-state electron spin polarizations and allows for determination of wavefunctions that give rise to the spin polarizations. This system is unique in that it requires neither intersystem crossing nor magnetic resonance techniques to create dynamic spin- and nuclear polarizations in molecules.

For each radical-appended D-A dyad, relaxation within the excited manifold to the lowest energy doublet excited state is followed by radiationless charge recombination back to the ground state. The lifetimes for these charge-separated excited states are correlated with the bridge fragment that separates the stable radical from the donor side of the D-A dyad. We will also show similarities in select electron-electron exchange couplings in our three-spin, charge-separated excited states with those in structurally-related ground-state biradicals, and how these exchange interactions effect excited-state lifetimes.





Spin-dependent mechanisms of charge transport along oligophenylene molecular wires

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Using a new efficient quantum mechanical method for modeling spin dynamics in radical pair reactions [1], we have studied magnetic field effects on the charge recombination process in donor–bridge–acceptor (D–B–A) molecular systems [2]. Specifically we model the charge recombination process in phenothiazine (PTZ) *p*-oligophenylene (Ph_n) perylene-3,4:9,10-bis(dicarboximide) (PDI) molecules, which have been studied experimentally by Weiss *et al.* [3]. By comparing the results of our simulations to the experimental data of Weiss and coworkers for the magnetic field effects on the PTZ-Ph_n-PDI radical ion pair charge recombination, we are able to extract spin-dependent recombination rate constants for a range of different PTZ–Ph_n–PDI molecules with different numbers n of phenylene groups in the bridge. These rate constants cannot be extracted directly from the experimental measurements because they require fitting simulated magnetic field effects to the experimental data. The extracted rate constants suggest that the singlet and triplet charge recombination processes proceed via different mechanisms. The triplet recombination rate is found to decrease exponentially with the phenylene bridge length, consistent with a superexchange charge recombination mechanism. The singlet recombination rate however is found to be approximately independent of the bridge length, suggesting this recombination is dominated by incoherent hopping. A simple qualitative explanation for the different behaviors of the two spin-dependent charge recombination pathways is provided in terms of Marcus theory. We also find evidence for a magnetic-field-independent background contribution to the triplet yield.

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Solutions for high-end research to routine analytical tasks

Sylwia Kacprzak

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One of the main drivers for new developments in EPR is the demand for higher signal-to-noise (S/N). With a number of recent and upcoming product introductions we have made significant progress in this field.

The high-power Q-Band pulse-EPR setup allows running DEER experiments with dramatically improved sensitivity: The measurement time of 22 h in X-Band is reduced to 25 min in Q-Band, thus increasing sample throughput by more than a factor of 50. To achieve this, a combination of a high-power pulse amplifier (150 W) and a large-volume resonator are used allowing short inversion pulses of 10 ns at 150 MHz resonator bandwidth.

Limitations in excitation bandwidth are a severe handicap in pulse-EPR. The availability of high-speed arbitrary waveform generators allows new methods in EPR based on pulse shaping for larger bandwidth excitation. With shaped broadband inversion pulses, the DEER modulation depth can be improved by a factor 2–3, and HYSCORE spectra can be measured with much higher S/N.

An ongoing project to substantially increase the S/N ratio is the development of a "rapid-scan unit". The direct registration of the EPR spectra via the rapid-scan method allows recording of absorption spectra, exciting the complete spectrum in a single shot. In addition, due to the short time during which the spins are exposed to microwave field, the saturation effect is less pronounced compared to cw-EPR. This allows the use of high microwave fields and consequently increases the signal amplitude.

Currently, a "direct rapid scan" (DRS) EPR accessory is being designed by Bruker to further extend the functionality and performance of ELEXSYS and EMX plus systems. The preliminary information about accessory specifications will be presented and its performance demonstrated with experimental results.

For routine analytical tasks in a commercial use, all technological advances have to be combined with a strong focus on usability. This is exemplified by the EMXnano bench-top spectrometer, which features full instrument calibration with respect to field and signal amplitude. Its dedicated workflows require from the user only little technical knowledge.

Magnetic field effect on carrier dynamics in organic solar cells

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Photovoltaics harvest energy from sunlight and are widely recognized as an essential component of future global energy production. The power conversion efficiency (η) for crystalline silicon solar cells has been already close to the theoretical upper limit (30%) [1,2]. However, η for organic solar cells (OSCs) is not high enough yet although organic semiconductors are environmentally safe materials permitting us to fabricate lightweight, flexible and low-cost photovoltaics more than Si-based cells. Figure 1 illustrates the mechanism for the photovoltaic effect in OSCs [3]. Primarily the absorption of the electron donor (D) by light results in the production of an excited state (referred to as exciton, ex). In organic materials the weak intermolecular interactions tend to localize ex on the molecules. The ex diffuses within the D domain until its lifetime, because the built-in electric field (E_{bi}) due to the different work functions of the cathode and anode of device is not sufficient and the dielectric constant (ε) of organic semiconductor is too low to break up the ex. Once the ex reaches at the interface with an electron acceptor (A), a fast electron transfer from D to A occurs, leading to an electron-hole (e-h) pair across the D|A interface that is sometimes called as a charge-transfer state because e and h are Coulombically bound due to low ε. The e-h pair may recombine into the ground state or dissociate to free e and h. Subsequently the separated free carriers are individually transported towards the different electrodes mainly by hopping with the aid of the E_{bi} because of narrow band widths of HOMO and LUMO. Finally, the carriers are collected by the electrodes and driven into an external circuit. Under typical device operation condition there are many η-reducing factors in the mechanism for OSC, such as narrow light absorption bands of D and A, insufficient dissociation of ex, effective recombination of e-h, low drift mobilities of e and h, contact resistance with electrodes and so on. Therefore development of highly efficient OSCs needs a deep understanding of the kinetics of excitons and charged carriers in real devices. Since some elementary processes include spin-selective kinetics of pairwise complexes, the photon-to-free-electron conversion in OSCs is a kind of playground for spin chemistry. This contribution will be devoted to introduce studies on magnetic field effects on the current for a single-junction solar cell using pentacene and C_{60} as D and A, respectively [4].

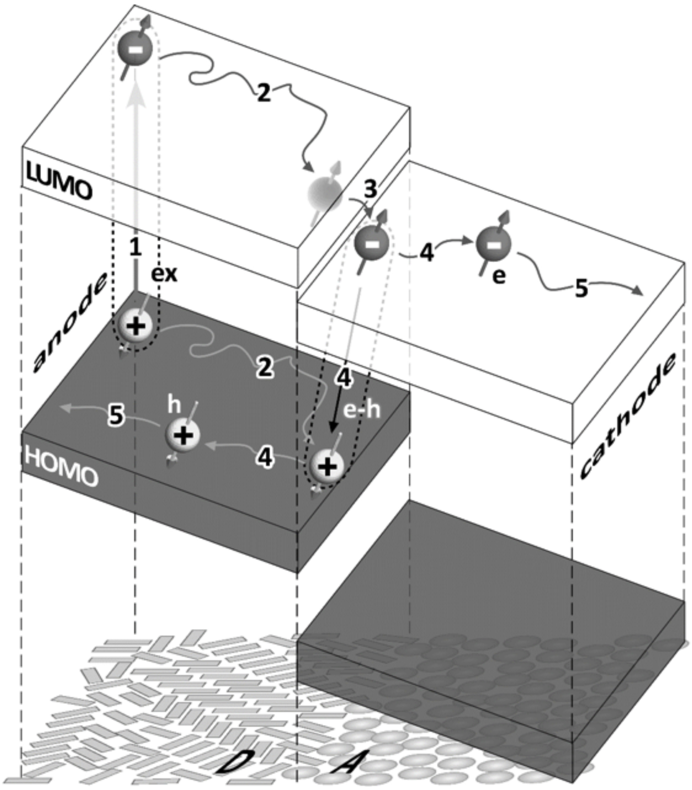

Figure 1: Schematic band diagram of a D|A interface in an OSC showing a viewpoint of (1) photoexcitation of an electron in the D-HOMO into the D-LUMO followed by (2) exciton diffusion to the interface, (3) electron transfer into the A-LUMO, (4) recombination and dissociation of the e-h pair, and (5) drift motion of the separated e and h away from the D|A-interface.

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Spin-dependent processes in organic solar cell materials

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Techniques based on electron paramagnetic resonance (EPR) spectroscopy can provide valuable insight into excitation transfer pathways in organic semiconductors used as absorber layers in solar cells [1]. However, these measurements are usually performed on "model systems", and the conclusions drawn from such experiments may not necessarily be valid under true solar cell operating conditions.

Here we report on the development of a setup that allows for simultaneous detection of transient EPR (trEPR) as well as transient electrically detected magnetic resonance (trEDMR) signals from fully-processed and encapsulated solar cells. Combining both techniques provides a direct link between photoinduced triplet excitons, charge transfer states and free charge carriers as well as their influence on the photocurrent generated by organic photovoltaic devices. Our results obtained from solar cells based on poly(3-hexylthiophene) and a fullerene-based electron acceptor show that the resonant signals observed in low-temperature ($T = 80$ K) trEDMR spectra can be attributed to positive polarons in the polymer as well as negative polarons in the fullerene phase, indicating that both centers are involved in spin-dependent processes that directly influence the photocurrent [2]. We will further show how electrically detected hyperfine sublevel correlation (ED-HYSCORE) spectroscopy can help to identify current-influencing paramagnetic states in organic tandem solar cells [3].

The second part of the talk will be devoted to triplet excitons, which are encountered in various materials used in high-efficiency organic solar cells. Triplet excitons can, on the one hand, be involved in loss mechanisms and reduce the yield of separated charge carriers. On the other hand, they play an important role in processes such as singlet fission that provide the possibility of building solar cells with quantum efficiencies exceeding 100%. Using trEPR spectroscopy, we study intermediate paramagnetic states generated upon fission of one singlet exciton into two separated triplet excitons. Particular emphasis will be given to strongly exchange-coupled triplet pairs in organic molecules that form quintet states [4].

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Structure and spin-dependent recombination of charge-transfer states in photovoltaic polymer/fullerene composites

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The key process in organic solar cell operation is charge separation under light illumination. When the active layer (typically, a blend of fullerene and a conductive polymer) absorbs light, an exciton is formed. It diffuses through the material until it decays to the ground state or reaches the donor-acceptor interface where the electron is transferred from the polymer to the fullerene. Thus, a charge-separated (CS) state is formed. Hereafter the CS state evolves into free charges with almost unity quantum yield for many polymer/fullerene blends. Due to the low dielectric constant of organic materials (about 3–4), the Coulomb attraction in the CS state is much higher than room temperature thermal energy. The understanding of the charge separation mechanism at the organic donor/acceptor interface still remains a challenge. To address this problem, the structure and the recombination of the CS state were studied by Q-band pulse EPR spectroscopy (electron-spin echo (ESE) detection).

Laser-flash induced echo-detected EPR spectra of the composites of different conjugated polymers with fullerene PC60BM were measured and analyzed. The spectra were obtained using the two-pulse microwave sequence $\pi/2 - \tau - \pi - \tau -$ echo immediately after the laser flash ($\lambda = 700$ nm) at a temperature of 40 K (delay after laser flash, 300 ns). The spectral shape is characteristic for a singlet-born spin-correlated radical pair, with some admixture of emission/absorption spin polarization [1]. It was found that the ESE intensity in the middle and on the edges of the spectrum depend differently on the microwave intensity. This is caused by relatively strong magnetic interaction (combination of exchange and dipolar interactions) between the spins of the positive and negative polarons constituting the CS state, which brings the radical pair away from the weak spin-coupling limit. From this dependence, the strength of the magnetic interaction of 5 MHz was estimated for the P3HT/PC60BM composite, which corresponds to an interspin distance of about 2 nm. It should be noted that the interspin distance distribution is broad for the CS state in polymer/fullerene composites, and the above value corresponds to its lower edge. The feature caused by strong magnetic coupling within the CS state dominates the flash-induced EPR spectrum for the poor-performing composites MEH-PPV/PC60BM and RRa-P3HT/PC60BM. It is less pronounced for the average-efficiency composite P3HT/PC60BM and almost disappears for the highly efficient composites PTB7/PC60BM and PCDTBT/PC60BM. Thus, the relative amplitude of the “anomalous” EPR feature can be used as a figure of merit for OPV materials.

The sign of the “anomalous” feature in the flash-induced EPR spectrum of the CS state inverts on the timescale of several microseconds at 40 K. Presumably this is caused by fast recombination of the CS state in the singlet spin state. At longer time, a triplet CS state with a much slower recombination rate dominates the flash-induced EPR spectrum.

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Triplet exciton loss channels in organic solar cells

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A strategy for increasing the conversion efficiency of organic photovoltaics has been to increase V_{OC} by tuning the energy levels of donor and acceptor components. However, this opens up a new loss pathway from an interfacial charge transfer state (CTS) to a donor triplet exciton (TE) state called electron back transfer (EBT), which is detrimental to device performance. To test this hypothesis, we study triplet formation in high performing blends of the fullerene $PC_{70}BM$ with either the polymer PTB7 [1] or the soluble small molecule *p*-DTS($FBTTh_2$)$_2$ [2] and determine the impact of the morphology-optimizing additive 1,8-diiodoctane (DIO). Using photoluminescence and spin-sensitive optically and electrically detected magnetic resonance (ODMR, EDMR) measurements we find that TE formation does not only depend on the materials' energetics, but also on temperature and nano-morphology. Furthermore, we observe TEs in real devices under realistic working conditions even for the most efficient solar cells, which has implications not only for efficiency, but also for device stability.

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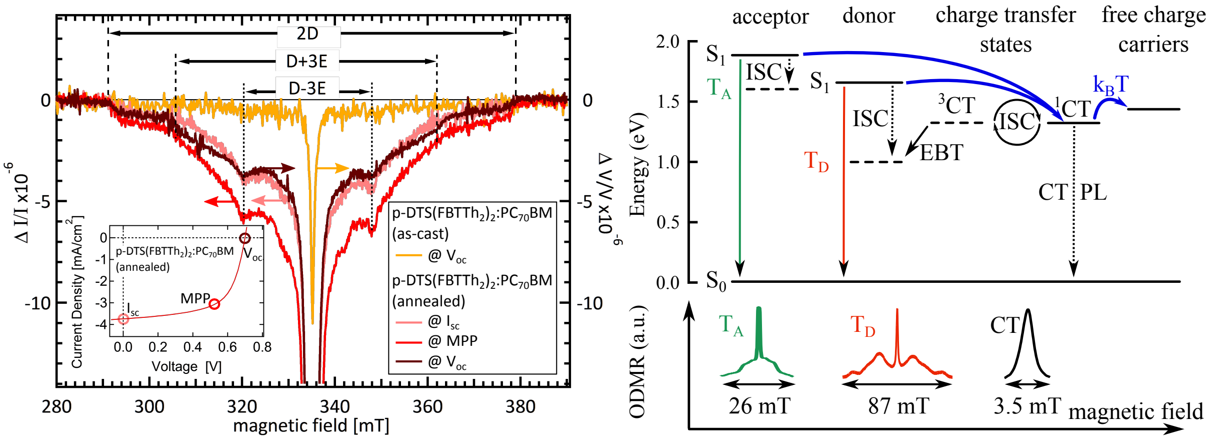

Figure 1: EDMR at different working points of an organic solar cell: V_{OC}, J_{SC}, MPP (left). Triplet excitons on *p*-DTS($FBTTh_2$)$_2$ formed by EBT (right).

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Not so free radicals

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In this lecture I will give an overview of time-resolved and steady-state electron paramagnetic resonance (TREPR and SSEPR) spectroscopies and their application in the study of radical structure, dynamics, and reactivity. I will emphasize the use of these techniques in probing chemical systems experiencing restricted translational or rotational motion. Examples of such systems include polymer coatings, structured fluids, microbubbles, nanocrystals, reverse micelles, and vesicles.

The TREPR technique is useful because it detects the primary photochemical events rather than rearrangements or secondary photolysis products. Examining radicals on the sub-microsecond time scale also allows us to examine the interplay between spin wave function evolution and diffusion in confined spaces ("spin chemistry").

In the second part of my talk I will demonstrate the use of TREPR and SSEPR in polymer degradation chemistry, the topology of singlet oxygen production in heterogeneous structures, such as vesicles and micelles, the photochemical "skunking" of beer by sunlight, biocompatible photopolymerization reactions, and the photoreactivity of sunless tanning lotions.

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Considerations to CIDEP of photolyzed inclusion compounds

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Host molecules of inclusion compounds such as cyclodextrines (CDs), calixarenes and crown-ethers are attractive to many different fields because of their specific properties of formation of host-guest complexes. These specific inclusion properties can be used for the purpose of molecular identification and separation. The host-guest complex formation is applicable to food preservation and also interesting to the fields of medical/pharmaceutical applications. For photo-chemists, these inclusion conditions are potential reaction fields for special photocatalytic reactions. Especially, the formation of a transient paramagnetic intermediate known as a radical pair (RP) in the sub-nanometer-sized confined space, which is the pathway for the consecutive reactions, is an attractive subject from the photo- and spin-chemical point of view.

Several papers have already been published on the photochemistry and spin-chemical aspects of frozen solutions of inclusion compounds at low temperatures [1−3] and aqueous solutions at room temperature [4,5]. These reports showed that the inside environment of CDs such as their bore size works for their specific properties. Our former report of the tr-EPR spectra obtained in the photolysis of aqueous solutions of sulfonated anthraquinones included in three CDs (α-CD, β-CD and γ-CD) [6] showed the chemical aspects such as the assignment of radical species and reaction dependence on the bore size of CDs.

In the present report, the data obtained in the former experiment [6] were reinvestigated. The quick quenching of TM (triplet mechanism) spin polarization, contribution of the hyperfine-dependent spin polarization of (S-T_-) RPM (radical pair mechanism), and nuclear-spin relaxation of the radical pair of these inclusion compounds are focused for discussion. These are controlled by the slow rotational correlation time of CDs and slow diffusional motion of the radical pair under the inclusion conditions. Details will be given in our presentation.

We thank Ms. Moe Sasaki, Ms. Rina Sato, Mr. Akira Naruoka, former students of Shizuoka University, for their enthusiastic help.

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Gigantic magnetic field effect on long-lived charge separated states created at a nonionic vesicle interface

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It is of much importance to create organic molecular systems that exhibit long-lived charge separated (CS) states or radical pairs upon photoirradiation for realization of artificial photosynthesis. In the field of spin chemistry, covalently-linked donor–acceptor (D–A) pairs [1] and non-covalent D−A pairs trapped in amphiphilic assemblies as micelles [2] have been the two main targets and extensively studied from the 1980s. The latter systems are advantageous in terms of ease and low cost of preparation over organic synthesis. However, the radical ion species created by charge separation tend to recombine or escape within $\approx 1\ \mu$s, which is problematic for application to photon-energy conversion. Because of this problem, the mainstream in the field of photochemistry shifted to fixed-distance covalent D−A systems, many of which exhibit long CS state lifetimes [3].

Despite this background, we have been studying electron and spin dynamics of non-covalent radical pairs created at the amphiphilic interface of surfactant-based assemblies. It turned out that fine-tuning the hydrophobicity of molecules allows us to control the dynamic behavior of generated radical species. For example, we have succeeded in creating a D−Chromophore (C)−A triad fixed at micellar interface, in which the C molecule acts as “dynamic charge transporter” to give a long-distance CS state with a lifetime of a few microseconds [4].

We have recently succeeded in creating a CS state of zinc tetraphenylporphyrin (ZnTPP) and dioctyl viologen (ocV^{2+}) at the interface of a nonionic vesicle (niosome), which exhibits a long lifetime of $\approx 3\ \mu$s at room temperature (Figure 1). It is noteworthy that the escape of generated radical species is negligible in contrast to the previously studied micellar systems. These observations indicate that the present non-covalent D−A pair behaves as if D and A are covalently connected. Furthermore, the “yield” of the CS state exhibits a gigantic magnetic field effect (MFE) over 100% at 250 mT. The MFE is sharply dependent on temperature and exceeds 250% at 6 °C. These CS state properties are advantageous for future applications such as magnetically enhanced artificial photosynthesis, photo and magnetically controlled drug delivery, and intracellular biosensors of temperature or magnetic field. Details in the mechanism of MFE and CS state dynamics will be discussed.

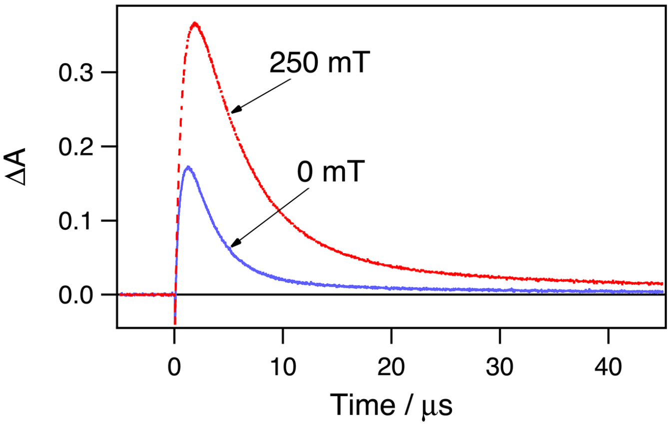

Figure 1: MFE on the transient absorption kinetics of the CS state [ZnTPP$^{+\bullet}$ ocV$^{+\bullet}$] created at a niosome interface at room temperature.

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Magnetic isotope effect in the environment. A study of mercury stable-isotope fractionation

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Soon after the first measurement of mercury (Hg) stable isotopes during the early 2000s [1], fractionation of the magnetic isotopes (measured as Δ^{199}Hg and Δ^{201}Hg) was observed in samples of biological tissue from around the world. Experimental [2] and field [3] evidence suggested that these anomalies are exclusive to photochemical transformations of Hg in aquatic media. The magnetic isotope effect (MIE) via the radical pair mechanism is widely assumed to be the cause of photochemical fractionation signatures, similar to the mechanism proposed for the fractionation of lighter elements (e.g., C, N, S) [4]. However, it has not been clearly demonstrated that the MIE is behind the observed Hg fractionation due to high spin–orbit coupling (SOC) and the chemical complexity and low viscosity of natural waters [4,5].

Here we investigate the MIE trends of Hg isotopes in (a) biological marine samples from the Atlantic and Pacific Ocean to survey for the global signatures of Δ^{199}Hg and Δ^{201}Hg, (b) deionized water and synthetic seawater containing low-molecular organic ligands and Hg species exposed to natural sunlight to investigate the sensitivity of Δ^{199}Hg signatures to reaction conditions, and (c) Hg photoreduction by photosynthetic marine phytoplankton (*Isochrysis galbana*) experiments to reproduce the isotopic trends observed in nature. From this interdisciplinary approach, we find (a) a global signature of the ratio of Δ^{199}Hg to Δ^{201}Hg equal to 1.2 ($R^2 = 0.99$; $n = 100$), which indicates a ubiquitous photochemical reaction; (b) a broad range in Δ^{199}Hg values (-0.6 to 6‰ [$n = 26$]), which indicated that photochemical transformations of Hg in biological tissue are sensitive to environmental factors; and (c), for the first time, that phytoplankton exhibit MIE intracellularly (Δ^{199}Hg = up to 3‰) with a fractionation pattern similar to those previously observed in nature [6]. Finally, we used *ab initio* quantum chemistry methods at the coupled-cluster level to explore the possibility of MIE by a radical pair mechanism in natural waters. We found that organic thiol-mercury complexes have excitation energies in the UVA region and the potential energy surface indicates a photodissociation mechanism.

The MIE signatures in this study suggest that a ubiquitous mechanism is responsible for the photoreduction of Hg and that a radical pair mechanism is driving the fractionation of ^{199}Hg and ^{201}Hg isotopes in aquatic environments. To conclude, we discuss MIE as a potential mechanism and highlight the limited understanding of the contributions of SOC and hyperfine coupling to the spin dynamics of metal complexes.

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Millitesla magnetic field effects on the photocycle of an animal cryptochrome

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Here we report the observation of magnetic field effects on the photo-induced electron transfer reactions in *Drosophila melanogaster*(*Dm*) cryptochrome. The magnetic sensitivity of these reactions is characterized by a combination of transient absorption spectroscopy and broadband cavity-enhanced absorption spectroscopy. Together, these techniques provide time-, field- and wavelength-resolved spectral data from which detailed insights into the photo- and radical pair chemistry of this blue-light photoreceptor protein are obtained [1].

We report that the radical pair kinetics differ markedly from those of closely related members of the cryptochrome-photolyase family. These differences and the magnetic sensitivity of *Dm* cryptochrome are interpreted in terms of the radical pair mechanism and a photocycle involving the recently discovered fourth tryptophan electron donor.

As the fruit fly has previously been shown to exhibit magnetosensitivity [2,3] in a variety of behavioral responses, this demonstration of a pronounced magnetic field effect on the isolated *Dm*Cry protein *in vitro* lends considerable weight to the hypothesis that the radical-pair mechanism is involved in the process of animal magnetoreception.

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Paramagnetic intermediate states in cryptochromes

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Flavin-dependent cryptochromes are evolutionarily related to the light-dependent DNA repair enzyme photolyase and serve as major regulators of, *e.g.*, circadian rhythms in insects and vertebrate animals. Paramagnetic states are intermediate redox states in these proteins, and hence, detailed knowledge of their chemical nature is required for a full understanding of their reactivity [1]. In this contribution, we use a number of (time-resolved) molecular spectroscopy methods to explore diverse reactions in cryptochromes, from primary events directly after light excitation to secondary light-independent reactions.

A number of examples will be presented: First, we were able to characterize dark and signaling redox states by in-cell steady-state EPR spectroscopy. Second, short-lived paramagnetic intermediates were characterized by time-resolved methods of all flavors [2]. Here, details in electron-transfer pathways could be revealed [3,4]. Finally, variants of *Drosophila melanogaster* cryptochrome revealed a number of potential signaling pathways.

The work presented here has been performed in collaboration with Kevin Henbest, Kiminori Maeda, Peter J. Hore, Christiane R. Timmel and Stuart Mackenzie from the Oxford University (Oxford, United Kingdom), and Stephanie Franz and Lars-Oliver Essen from the Philipps-Universität Marburg (Marburg, Germany).

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Behavioral evidence for the orientation of rice planthopper Nilaparvata lugens using a magnetic cue

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Progress has been made in understanding the mechanisms underlying directional navigation in migratory insects, yet the magnetic compass involved has not been fully elucidated. Here we developed an experiment to study the route directionality of the migratory rice planthopper *Nilaparvata lugens* in response to magnetic fields and the influencing factors of the orientation. Planthopper adults were trained successfully to find the food source, which was put inside Helmholtz coils and light was provided. After 10 hours the insects gathering around the food were collected and re-put in the Helmholtz coils for recording the number of the insects in four directions.

Three groups under the local inclination (Beijing, China) of 0.1 mT magnetic field with food resource in north, west and east were tested respectively. The result showed that most of the insects distributed in north in all of the three test groups. As the group with food in north was the most significant, the rest of the experiments was done under this food direction. In the following, the horizontal component or vertical component of the direction of the magnetic field were changed. The results indicated that when the vertical component was reversed, most of the insects were unable to visit the former direction.

For the influencing factors of orientation, two experiments were designed. In the first experiment, the insects were raised in 1 mT magnetic field and the control were raised in geomagnetic field. In the second experiment, the putative magnetoreceptor gene (*magr*) in rice planthopper was silenced with the control of wild type. Compared with the control, the amounts of the insects with silenced *magr* visiting the former direction declined significantly.

This experiment indicates that the route orientation of the rice planthopper *Nilaparvata lugens* is affected by the inclination of the local magnetic field, and the putative magnetoreceptor MagR may have an effect on its orientation.

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Molecular insights into electron transfers in cryptochrome

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The photoreceptor protein cryptochrome is thought to host, upon light absorption, a radical pair that is sensitive to very weak magnetic fields, endowing migratory birds with a magnetic compass sense. The molecular mechanism that leads to formation of a stabilized, magnetic-field sensitive radical pair has despite various theoretical and experimental efforts not been unambiguously identified yet. We challenge this unambiguity through a unique quantum-mechanical molecular-dynamics approach where we perform electron transfer dynamics simulations taking into account the motion of the protein upon the electron transfer. This approach allows us to follow the time evolution of the electron transfer in an unbiased fashion and to reveal the molecular driving force that ensures fast electron transfer in *Arabidopsis thaliana* cryptochrome guaranteeing formation of a persistent radical pair suitable for magnetoreception [1]. We argue that this unraveled molecular mechanism is a general principle inherent to all proteins of the cryptochrome/photolyase family and that cryptochromes are, therefore, tailored to potentially function as efficient chemical magnetoreceptors.

We further extent our analysis for *Xenopus laevis* cryptochrome DASH, where recent experimental studies [2] have shown that even if some of the amino acids in the active site are mutated, radical pair formation is still observed. We employ dynamical quantum mechanical calculations [3] to study this phenomenon in molecular detail by first constructing a homology model of *Xenopus laevis* cryptochrome DASH, and then mutate key amino acids involved in the electron transfer. We report several new alternative electron transfer pathways resolved at the molecular level, consistent with experiment, and compare the amino acid sequences of different cryptochrome species to show that one of the alternative electron transfer pathways could be general for all cryptochrome DASH proteins.

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Radical-pair based magnetoreception amplified by radical scavenging

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Birds have a remarkable ability to obtain navigational information from the Earth's magnetic field during their long migratory voyages. The primary detection mechanism of this compass sense is uncertain but appears to involve the quantum spin dynamics of radical pairs formed transiently by photo-induced electron transfer reactions in the flavoprotein cryptochrome. It is puzzling that in many respects the compass performance in animals surpasses the predictions of model calculations [1], suggesting the presence of a powerful, yet unknown, amplification process. This prompted us to seek quantum and classical amplification mechanisms [2,3]. Here, we report on a surprising effect associated with spin-selective reactivity that can vastly enhance the performance of the quantum magnetic compass.

Based on model calculations, we propose a new mechanism of magnetoreception in cryptochromes that features a spin-selective electron transfer reaction of one of the radicals of the primary pair with spin-bearing scavenger (chemical Zeno effect) [4,5]. The new scheme offers clear and important benefits such as a greatly enhanced sensitivity to a $50\,\mu$T magnetic field (by up to two orders of magnitude in the relative anisotropy) and magneto-sensitivity for radicals that are more than 2 nm apart. This means that radical pairs that are too far apart to undergo spin-selective recombination reactions could also be viable magnetic compass sensors and that the detrimental effects of inter-radical exchange and dipolar interactions can be minimized. Even more surprisingly, the effect immunizes the sensor to fast decoherence processes in one of the radicals. As a consequence, magnetic field effects of radical pairs involving swiftly spin-relaxing species, such as superoxide, are no longer be precluded.

Eventually, radical scavenging can also be applied to isotropic magnetic field effects, for which it can markedly boost the size of the low-field effect.

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Testing the cryptochrome hypothesis of magnetoreception: a 'killer' experiment?

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It is now nearly 40 years since the delicately balanced evolution of spin states in radical pair reactions was first suggested to underlie the remarkable ability of migratory birds, among other animals, to detect the Earth's weak magnetic field [1]. Investigation of the theory eventually took off in earnest in 2000, when the photoreceptor cryptochrome was proposed as the source of the magnetically sensitive radical pairs [2]. However, despite mounting behavioural, neurophysiological, spectroscopic and theoretical support, conclusive evidence for a cryptochrome magnetoreceptor remains elusive [3,4]. Genetic knockout studies on *Drosophila melanogaster* [5] provide the strongest argument for the involvement of cryptochrome in magnetoreception but even these experiments cannot tell whether it truly acts as a magnetoreceptor or as an upstream or downstream signal transducer.

The lack of a definitively identified receptor presents significant obstacles in the search to understand and confirm the radical pair mechanism of animal magnetoreception: simulations of the system cannot be confidently parameterized, the criteria for a functioning compass cannot be rigorously explored, and appropriate conditions cannot be methodically sought *in vivo*.

We propose an experiment that could convincingly test whether or not a cryptochrome-based radical pair is truly responsible for avian magnetosensitivity. The key to this experiment is using a superparamagnetic nanoparticle to selectively disrupt the coherent spin evolution of the cryptochrome radical pair, without otherwise affecting the ability of the protein to participate in magnetic sensing, *e.g.*, as part of an electron transfer pathway. We have used model calculations to explore the efficacy of Néel relaxation and Brownian motion of the nanoparticle in altering the ratios of singlet and triplet radical pairs (and hence the production of a signaling state) and to determine both the necessary and optimal magnetic characteristics for the nanoparticle. Candidate nanoparticles have been identified that fulfil these requirements and their effect on the cryptochrome compass has been demonstrated using more realistic models. Finally, we consider the practical challenges of implementing this experiment and suggest ways that they might be overcome.

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Radical pair spin lifetime and dynamics studied by static and pulsed magnetic field

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Magnetic field effects (MFEs) on the photochemical reactions of flavin-containing systems are getting great attention based on the interest in the magnetoreception of blue-light receptor proteins [1] for animal navigation. Recently, microscope-based detection of MFEs was developed targeting flavin-containing biological systems [2,3]. In them, the photo-induced intramolecular electron transfer reaction of FAD was used to test the equipment. The photo-induced intramolecular reaction of FAD has a unique interconversion between the triplet excited state (T) and the radical pair (RP) [4]. Therefore, reaction kinetics of the system are hardly measured only by time resolved spectroscopy because it is under the quasi equilibrium condition of RP and T. However, the reaction kinetics of the RP could be analyzed by precise analysis of MARY (magnetic field effect on reaction yield) spectra. Here we present newly developed time-resolved MARY in laser-flash photolysis using a very stable diode-pumped pulse laser. The time-resolved MARY with very high S/N ratio is shown in Figure 1A. The time evolution of the linewidth ($2\,B_{1/2}$) reflects the spin dephasing and the lifetime of RPs, which is manifested in SLE (stochastic Liouville equation) based theoretical model calculations as shown in Figure 1C.

We have also studied the effect of a pulsed magnetic field [5] in the laser-flash photolysis of 2,6-AQDS (anthraquinone 2,6-disulfonate) and hen egg white lysozyme (HEWL) [6]. The two-phase decay components of the radical pair on the surface of the protein can be discussed by the binding feature of 2,6-AQDS in the ground state, which is obtained by UV/vis spectroscopy.

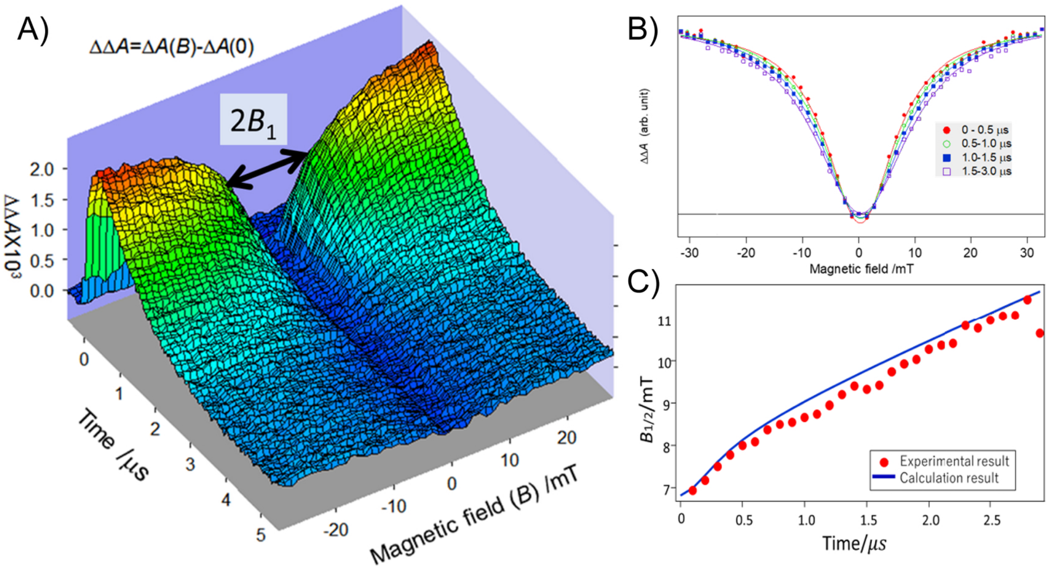

Figure 1: (A) Time-resolved MFE spectrum (2D-MARY), (B) magnetic-field slices at different times, and (C) time evolution of $B_{1/2}$ obtained by Lorentzian fitting of the spectra and the theoretical fitting by SLE calculations.

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Magnetic field effect. An assessor of donor–acceptor separation in photoinduced reaction

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We like to design simple experiments to unravel the role of structure of participating molecules and the solvent matrix on inter- and intra-molecular electron/proton transfer and hydrogen abstraction between therapeutically important small molecules and biological macromolecules using steady-state and time-resolved spectroscopic techniques, magnetic field effects and theoretical modeling. Although the steady-state and time-resolved absorption and fluorescence help to identify the ultimate products and transient intermediates respectively, the importance of magnetic field effect lies in its ability to identify the initial spin state, one of the deciding factors for ultimate products, as well as to assess the intermediate distance in geminate spin-correlated radical ion pairs/radical pairs produced as transients, which is very useful to study 'distance-dependent' interactions in macromolecules. The transient geminate radical ion pairs with the spin correlation like parent electronic state produced through photoinduced electron transfer undergo intersystem crossing between degenerate $S \leftrightarrow T_0$, $T_\pm$ states through hyperfine interactions and it becomes most favorable when the component radical ions are separated by a certain distance where the exchange interaction becomes negligible. Application of an external magnetic field of the order of hyperfine interactions reduces the intersystem crossing by Zeeman splitting leading to an increase in recombination product or free ion formation when the initial spin state of the radical ion pairs is singlet or triplet respectively. Moreover the magnetic field effect is maximized at an inter-radical distance of ≈ 10 Å, which is also the optimum distance for efficient electron transfer. Recently we have found that this is also applicable to electron transfer between amine passivated highly complex structured carbon dots chemically modified with homocysteine thiolactone and a model anticancer drug, menadione in physiological condition [1,2]. However, the use of ferromagnetic iron nano particles can induce high field effects instead of low field hyperfine interaction while making complex with the photo-excited molecule.

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Magnetic field effect anisotropy. A chemical compass in the low field region

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It is well known that many migratory birds use the magnetic field of the Earth to navigate. The exact details of the underlying field sensing processes are unknown, however, and several possible mechanisms have been suggested [1]. One of the most likely candidates [2] is based on the well-established radical pair mechanism (RPM) [3,4]. Here, the kinetics of a photo-induced radical pair reaction are altered by the amplitude and orientation of an applied magnetic field. The underlying quantum mechanical process of singlet-to-triplet interconversion is very sensitive to the specific characteristics of the chemical system in question. It is, *e.g.*, dependent on the distance between the involved radicals, the coupling between the electron and nuclear spins within each radical, their orientation in the magnetic field, and environmental conditions such as the solvent. Studies on the protein(s) suggested to be involved in magnetoreception *in vivo* are challenging; especially orientation and low-field effects are expected to be small and hence require exquisite sensitivity of the experimental apparatus. It is thus attractive to understand many of the underlying phenomena using model systems which can be custom-synthesized and chemically engineered to test for the influence of hyperfine couplings and/or radical pair lifetimes.

Here, we present transient absorption spectroscopy measurements on such a model system, a carotenoid–porphyrin–fullerene triad [5]. We observe that the singlet-to-triplet interconversion rates can indeed be altered by changing the direction of an externally applied field for field strengths as low as 100 μT. The experiments thus serve as a proof-of-principle for chemical compass systems in the so called “low field region”, accessible to birds. Furthermore, future measurements on chemically modified triad molecules could allow further insight into the fundamental aspects governing such magnetic field effects (MFEs), and could serve as a promising starting point for the development of other artificial chemical compass systems.

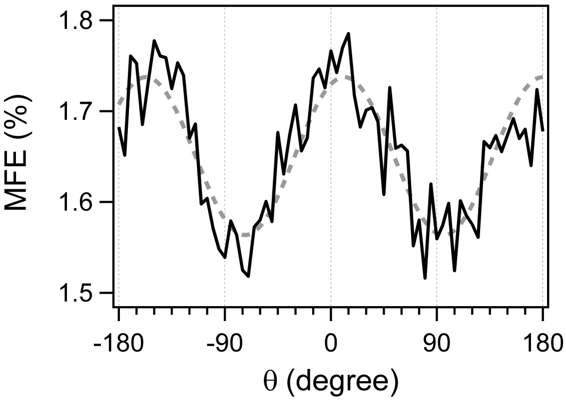

Figure 1: Variation of MFE with changing angle between molecular axis and a magnetic field of 100 μT, 0.08 μs after laser excitation (black); molecular axis and field are parallel for $\theta = 90°$; sinusoidal fit to the data (dotted grey).

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Engineering an artificial flavoprotein as a model for radical pair-based magnetosensors

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It is well established that certain birds and insects use Earth's magnetic field for navigation. This magnetic compass sense is light dependent, and it is hypothesized to be facilitated by cryptochromes: a class of proteins containing flavin adenine dinuclotide (FAD) and a tryptophan (Trp) chain. Upon light activation, electron transfer between the FAD and Trp forms a spin-correlated radical pair, the lifetime of which is sensitive to applied magnetic fields [1]. While there have been several successful studies demonstrating the magnetic sensitivity of Cry and related proteins, the fine details of the magnetically sensitive chemistry can be obscured by the inherent complexity or overlapping functions of the native proteins [2,3]. In order to better understand the functional requirements of this complex molecular compass, we have designed a simple *de novo*, protein-based model system – known as a flavomaquette – that contains a covalently bound flavin and a single Trp residue. Optical and cavity-enhanced absorption spectroscopies were used to explore photophysical behavior of these maquettes as a function of the distance between the flavin and Trp [4]. Electron transfer observed in the flavomaquettes leads to the formation of a magnetically sensitive radical pair. Despite bearing no structural resemblance to the native Cry fold, a strong magnetic field effect that rivals natural systems is observed in the flavomaquettes at room temperature. This is the first example of an artificial protein magnetosensor. The maquette structure offers unprecedented freedom in modifying their design in order to explore the basic requirements of magnetoreception in a protein environment. Recent work has taken advantage of this versatility by modifying the basic maquette sequence to incorporate multiple amino acids that build towards Trp-based, electron transfer chain like that in Cry and by substituting different amino acids (tyrosine) with the goal of improving the driving force for electron transfer and spectrally resolving individual electron transfer steps.

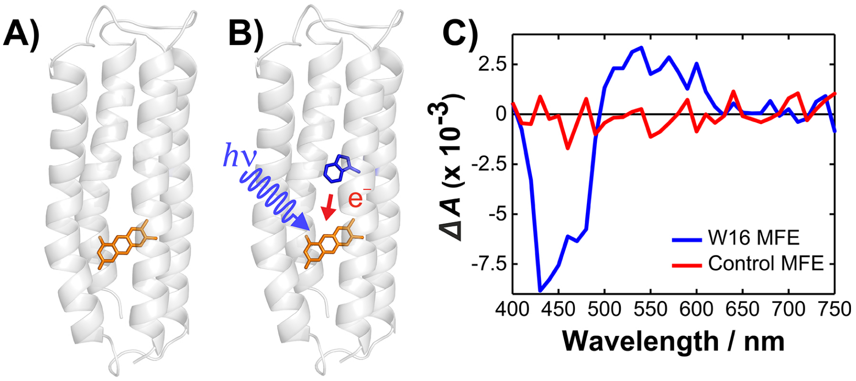

Figure 1: Representation of a control maquette (A) in which electron transfer does not take place and a functional maquette (W16, B) containing a flavin and one Trp residue. A large, room-temperature magnetic field effect (C) is observed in these proteins using transient absorption spectroscopy.

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Microspectroscopic studies of flavin-based radical pairs

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It has long been known that radical pairs (RPs) are able to imbue chemical reactions, in which they participate as intermediates, with sensitivity to externally applied magnetic fields. Remarkably, despite this fact and the ubiquity of free radical intermediates in biologically important reactions, there has, to date, been little evidence for direct magnetic field effects on biological reactions that has stood up to extended and careful scrutiny. However, the recent wealth of evidence that has been amassed over the ability of a wide range of animal species to respond to the geomagnetic field has helped to focus the direction of spin chemists interested in biological magnetic field sensitivity. A range of evidence from a number of different sources strongly suggests the role of cryptochromes in the magnetic sensing ability of many species and, indeed, the photochemistry of some purified cryptochromes *in vitro* has been shown to be magnetically sensitive [1,2]. With regard to the biological sensing mechanism, many unanswered questions remain, not least over how animals can detect, with sufficient sensitivity, the direction of a magnetic field as weak as the Earth's.

Key to the current thinking on the cryptochrome RP-based hypothesis for animal magnetoreception is the molecule flavin adenine dinucleotide (FAD), a non-covalently bound cofactor in cryptochromes. In fact, important questions exist over whether FAD is actually even bound in type-II cryptochromes [3], typically found in animals (it is confirmed to be bound in type-I cryptochromes, present in plants). Remarkably, on its own in solution, FAD's own cyclic photochemistry shows a substantial magnetic field response, which even extends to the presence of a low field effect (LFE) [4]. FAD photochemistry (and its response to applied magnetic fields) is highly dependent on its conformation, which can be controlled both in solution (*e.g.*, by pH), and when bound to proteins (based on the FAD–protein non-covalent interactions and binding site structure). Therefore, experimental tools to investigate FAD photochemistry and its magnetic field response in a wide range of different locations, from isotropic solution, through controlled structured and biomimetic environments to living cell apparatus, are highly desirable.

We have developed microscopic imaging spectroscopic methods for the observation of RP dynamics on sub-micrometer length scales, based on both emission and absorption spectroscopies. For example, transient optical absorption detection (TOAD) imaging allows direct observation of short-lived free radicals and magnetic field effects thereon while magnetic intensity modulation (MIM) imaging directly observes regions of space containing magnetically sensitive chemical reactions. These techniques are capable of providing spatially resolved information where necessary (for example inside cell apparatus and localized biomimetic micro-reactors) but can alternatively be employed for non-spatially resolved spectroscopy on very small volume samples with high sensitivity. Here we discuss instrumental aspects of such measurements, along with photochemical and magnetic field effect measurements of flavin-based RP reactions in a number of different reaction environments.

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New avenues in photochemically induced dynamic nuclear polarization in liquids

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) is a well-known phenomenon that has often been exploited in the context of nuclear magnetic resonance (NMR) to detect solvent-exposed regions of complex molecules and to assess electron transfer rates [1–5]. More recently, photo-CIDNP has emerged as a powerful hyperpolarization tool due to its ability to transiently perturb unfavorable nuclear-spin distributions and thus significantly enhance NMR sensitivity [6–9].

This lecture will discuss general principles underlying the photo-CIDNP process in liquids at high field. The role of extrinsic and covalently bound photosensitizer dyes, triplet states, radical pairs and geminate/F-pair recombination in the historical development of photo-CIDNP will be discussed [9]. Special emphasis will be placed on discussing how photo-CIDNP enhancement in the context of heteronuclear correlation spectroscopy enables NMR data collection at unprecedented sensitivity, down to the micromolar to low-nanomolar concentration range [10]. The presentation will include experiments and kinetic simulations showing how moderate amounts of new photosensitizer dyes mediate the collection of photo-CIDNP NMR data at sub-micromolar sample concentration in only a few seconds [10–12]. In addition, the lecture will show how cryogenic probe technology is compatible with photo-CIDNP, leading to ultra-rapid NMR data collection in dilute samples. Finally, the presentation will include additional ongoing developments specifically tailored to further enhance NMR sensitivity via photo-CIDNP.

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The solid-state photo-CIDNP effect

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The solid-state photo-CIDNP effect occurs in spin-correlated radical pairs under solid-state conditions at specific magnetic field strengths upon illumination with light. The effect allows for detailed studies of such radical pairs, occurring for example in photosynthesis and assumably animal navigation. The spin-chemical machinery leading to dramatic nuclear hyperpolarization is explored. Present developments will be presented.

The theory has been re-established in terms of level (anti-)crossings [1], and there has been an attempt to explain principles of spin chemistry to the spintronics community [2].

New photosynthetic systems, even from a new kingdom, the kingdom of diatoms, have been demonstrated to show the effect [3]. In classical reaction centers of *Rhodobacter sphaeroides*, an entirely ^{13}C labelled sample was analyzed by time-resolved photo-CIDNP MAS NMR experiments [4].

There is also substantial progress in adapting advanced MAS NMR pulse schemes, such as INADEQUATE, in photo-CIDNP MAS NMR experiments [5] allowing to improve chemical-shift assignments.

Also a blue-light photoreceptor protein has been analyzed by photo-CIDNP MAS NMR [6]. Recently, a synthetic model compound for natural cryptochrome has been presented and with various optical and magnetic resonance methods tested [7,8].

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Exploiting radical–triplet pair hyperpolarization for sensitivity enhancement in solution-state NMR

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NMR is intrinsically insensitive due to the low thermal spin-polarization of nuclei, limiting both routine applications and development of new methodologies; the hyperpolarized states with which spin chemistry deals therefore have much to offer. The use of optically generated electronic hyperpolarization arising through a radical pair mechanism to provide selective NMR signal enhancements in photo-CIDNP is already well known [1]. Here we present our recent demonstration of an alternative method (Figure 1), using electronic hyperpolarization arising through a radical-triplet pair mechanism (RTPM) to provide bulk sensitivity enhancements in solution-state NMR [2]. Whereas photo-CIDNP relies upon a spin-selective reaction of a photogenerated triplet with for example specific amino acid residues (typically Tyr, Trp and His) the RTPM can hyperpolarize extrinsic stable radicals. Cross-relaxation transfers electronic polarization from radicals to coupled nuclei, resulting in NMR signal enhancements, as already exploited in Overhauser dynamic nuclear polarization (DNP) [3]. DNP methods typically involve driving polarization transfer by microwave pumping of electronic transitions, with maximum enhancements limited by the thermal electron-spin polarization. Hyperpolarizing the electron spins by optical pumping could offer much larger enhancements, overcoming the Boltzmann limit, and also removes the need for technically demanding microwave irradiation as once hyperpolarized the electrons undergo cross-relaxation without any further driving radiation.

Alongside our proof of principle demonstration of RTPM enhanced NMR [2] we report recent progress in optimizing the method. Combining time-resolved EPR investigations with recent kinetic studies [4] we have further developed our understanding of the radical-triplet pair system. Correlating this data with NMR measurements we have identified the conditions that maximize the DNP enhancement, and have exceeded our previous record despite also moving away from costly deuterated solvents.

Acknowledgements: We thank the UK's Engineering and Physical Sciences Research Council for financial support (EP/N007875/1), and Bruker UK for an equipment loan.

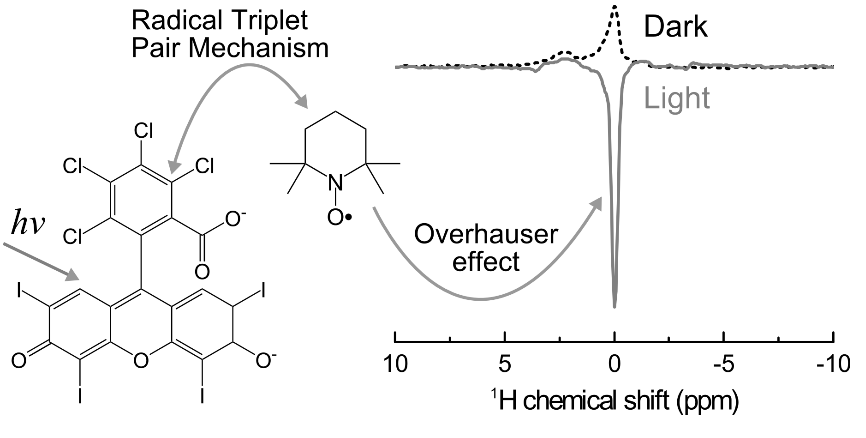

Figure 1: An optically generated triplet state hyperpolarizes a stable radical, which due to cross-relaxation leads to enhanced ^{1}H-NMR sensitivity in aqueous solution.

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Competition of singlet and triplet recombination of radical pairs in photoreactions of 3,3′,4,4′-tetracarboxy benzophenone with biologically important molecules

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Photoinduced electron transfer serves as a versatile method for generating elusive radicals of biologically important molecules. It is of great importance to use a well characterized water-soluble organic triplet photosensitizer that efficiently reacts with the compounds of interest. In our work, 3,3′,4,4′-tetracarboxy benzophenone (TCBP) was chosen because of its high intersystem crossing quantum yield and high reactivity of the excited triplet state [1,2], with the additional advantage of good solubility in aqueous solution over a wide pH range. However, when using TCBP as a photosensitizer, we detected a rather unusual chemically induced dynamic nuclear polarization (CIDNP) kinetic behavior for the protons of the species participating in the photoreactions. In particular, during free diffusive collisions of radical pairs (so called F-pairs) consisting of the TCBP radical and the radical of an aromatic amino acid (tyrosine, histidine, or tryptophan), apparent polarization formation was much less efficient than in the standard case of a triplet precursor and recombination from the singlet state of the radical pair, which is typical for other triplet sensitizers. The time evolution of CIDNP for the protons of TCBP was completely different from that of all sensitizers studied earlier. This unusual CIDNP kinetic behavior was explained by the presence of a triplet recombination channel of the radical pairs along with the singlet one and that both channels contribute to nuclear polarization. It leads to the formation of the amino acid in its ground state and TCBP in a triplet state of low energy. This low-lying triplet of TCBP, the presence of which was also confirmed by transient absorption measurements, is characterized by its relatively long lifetime of 1 ms or longer. Taking into account such a triplet recombination channel allowed us to obtain excellent agreement of experimental and simulated CIDNP kinetics. In the simulation, we utilized the analytical solutions obtained for the ratio between CIDNP formed upon geminate and bulk recombination of radical pairs with singlet and triplet competitive channels of recombination (usually denoted as γ) [3]. The γ-value was computed for an arbitrary spin multiplicity, singlet or triplet, of the precursor as well as for arbitrary recombination rate constants of radical pairs in singlet and triplet states, k_S and k_T, respectively [3]. Thus, we established that the triplet back electron transfer is a key factor that governs the kinetic behavior of CIDNP at the photoreaction between TCBP and biologically relevant molecules in aqueous solution.

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NMR detection and characterization of transient reaction intermediates

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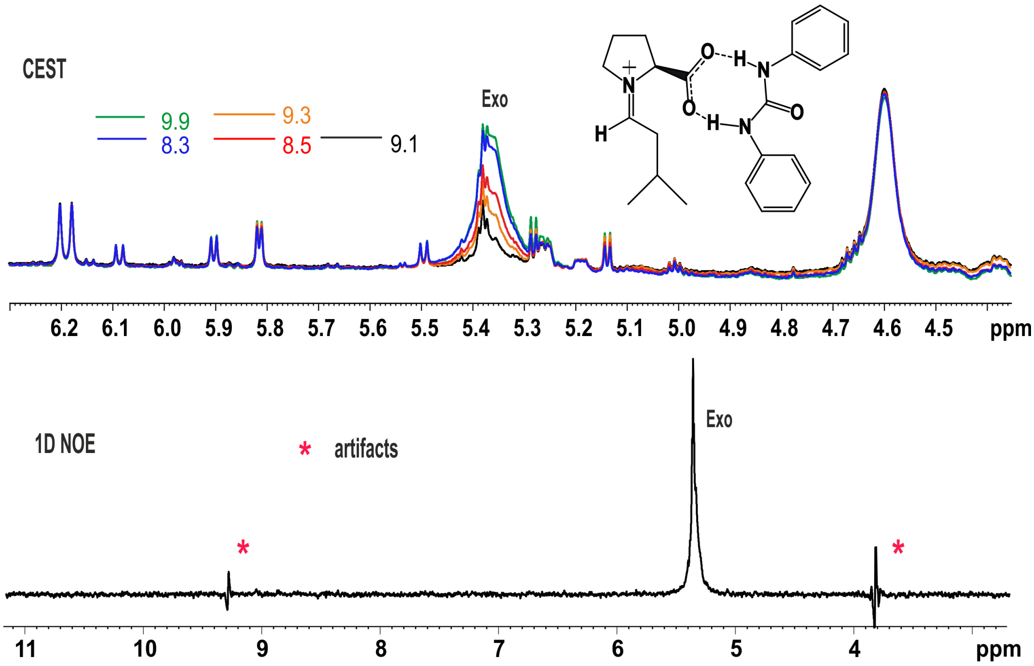
Understanding reaction mechanisms is absolutely essential to influence chemical reactions in order to achieve higher yields, greater selectivity and to accelerate reactions. In solution, NMR provides structural insight on intermediates, such as the presence of inter-molecular complexes, possible inter-molecular distances, the existence of hydrogen bonds, shortenings/stretchings of bonds and molecular binding modes. But most often reaction intermediates are transient in nature and remain unobserved by conventional NMR due to the inherent insensitivity of the technique, thus restricting its applicability to fractions of reactions. Here we report first detection of such transient intermediates by chemical exchange saturation transfer (CEST) NMR. The advantage of an amplified signal in the technique is exploited to observe iminium species in a proline enamine system, which were not detected earlier. CEST allows detection, quantification and the study of kinetics of low populated *Z*-iminium at 250 K. It is observed that *Z*-iminium is in slow exchange with *exo*-oxazolidinone on the NMR timescale. A significant downfield shift of *endo*-oxazolidinone on decreasing temperature and addition of N,N'-diphenylurea show that *E*-iminium is in fast exchange with *endo*-oxazolidinone on the NMR timescale. The obtained experimental results are comparable with theoretical results, which shows a lower activation barrier for *endo*-oxazolidinone to *E*-iminium than for *exo*-oxazolidinone to *Z*-iminium.



Decrease of intensity for *exo*-oxazolidinone peak in CEST NMR spectra shows the presence of *Z*-iminium. 1D-NOE failed to detect *Z*-iminium.

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Harnessing parahydrogen as a source of hyperpolarization

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Hyperpolarization turns typically weak NMR and MRI responses into strong signals so that ordinarily impractical measurements become possible. The potential to improve analytical NMR, clinical diagnosis and the study of reactivity through this approach reflect significant opportunities to improve scientific understanding. This presentation will discuss the methods that are available to use the low-cost parahydrogen approach. It will include illustrations that demonstrate it is possible to follow chemical transformations through the detection of true reaction intermediates whilst quantifying their role. The recent signal amplification by reversible exchange (SABRE) [1] will be described with studies on a series of biologically relevant nicotinamides and methyl nicotinates detailed [2]. Optimized procedures involving specific ^{2}H labelling in both the agent and catalyst will be shown to deliver polarization lifetimes of ca. 2 minutes with 65% polarization levels being attained. The use of a biphasic approach to deliver a saline-based biocompatible bolus without catalyst contamination will be discussed [3]. Furthermore, a series of *in vivo* ^{1}H MRI images will be presented. As a 1.5-T hospital scanner has an effective ^{1}H polarization level of just 0.0005%, this strategy should ultimately result in compressed detection times for chemically discerning measurements that probe disease. Related approaches to create hyperpolarized singlet states, shared between pairs of either ^{1}H or ^{13}C nuclei will reveal how it is possible to produce magnetic-state lifetimes that exceed 250 seconds [4].

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Next-generation coherent methods for efficient molecular hyperpolarization

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The most common hyperpolarization method (dynamic nuclear polarization) can dramatically increase magnetization in virtually any organic molecule, but the apparatus is complicated and expensive (ca. 2.5 M$ for clinical systems) and polarization grows slowly. Another approach, signal amplification by reversible exchange (SABRE), was conceived about a decade ago to directly polarize protons [1]. We extended this a few years ago in SABRE shield enables alignment transfer to heteronuclei (SABRE-SHEATH) to directly polarize heteroatoms, such as ^{15}N, using an extremely simple low-field apparatus [2]. Both methods use reversible binding of parahydrogen and target ligands to an iridium complex, and select a field where level anticrossings create magnetization in the target (and orthohydrogen). These papers have led to a wide range of applications: our group alone has polarized about fifty different reagents, including many that are biologically interesting [3]. In addition, we have shown that we can generate p-$^{15}N_2$, which is expected to be extremely stable and biocompatible.

SABRE and SABRE-SHEATH are inexpensive, general, and simple, but they have a few current limitations; the most significant is that hyperpolarization levels are typically lower than in DNP. However, both of these approaches are incoherent methods: the level anticrossings, combined with rapid exchange, simply saturate the polarizing transition. Here we demonstrate two new coherent approaches for creating significantly larger magnetization. In coherent SABRE, we pulse the low matching field for a precise interval to cause a *coherent* transfer and produce very substantial magnetization enhancements. Figure 1 shows the ^{15}N magnetization induced in acetonitrile by moving the field to the exact SABRE-SHEATH resonance for x ms, moving it off resonance for $(150 - x)$ ms, and repeating many times. The case of $x = 150$ ms (the right side of the curve) corresponds to normal SABRE-SHEATH. Magnetization flows through $^2J_{NH}$ couplings with a predicted near-complete transfer at 20 ms, so pulsing the field (and then allowing time for exchange) generates large signal increases – 150% increase in our first experiments. Theory and experiment are in excellent agreement (Figure 1) and the approach also lets us unravel important details about the magnetization transfer process, including the presence of inactive or magnetization-depleting states in the catalytic process. These insights have also let us drastically improve "low-irradiation generation of high Tesla SABRE" (LIGHT-SABRE) [4], which generates hyperpolarization *directly in a high-field magnet*; previous work was limited by susceptibility variations, but now is just as efficient as the low-field methods and much more convenient. Extensions to more complex field profiles will be discussed.

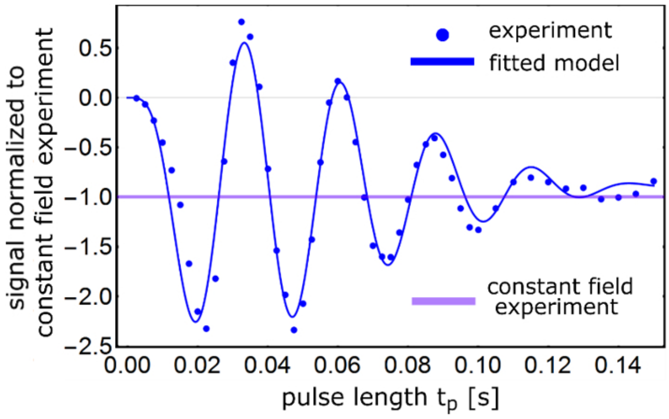

Figure 1: Coherent SABRE-SHEATH intensity *versus* pulse length in acetonitrile (experimental, dots; simulated, solid line). The field is cycled between the correct SABRE-SHEATH matching field and a mismatched field, with the sequence repeated after 150 ms. The maximum occurs at much shorter times, because scalar couplings across the iridium bond cause coherent transfer, in this case with more than double the magnetization.

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Hyperpolarization chemistry for applications ranging from chemical analysis to affordable molecular imaging

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The presented research focuses on combining low-cost hyperpolarization and low-cost, low-field NMR and MRI to deliver ultrasensitive and affordable chemical analysis and biomolecular MRI. First, we develop and characterize parahydrogen-based polarization transfer catalysis, which we use to hyperpolarize metabolites, drugs and other small molecules directly in room temperature solutions (organic and aqueous) [1–4]. In particular, we use SABRE-SHEATH (signal amplification by reversible exchange in shield enables alignment transfer to heteronuclei) to hyperpolarize substrates, which are designed with heteronuclear (^{15}N and ^{13}C) spin labeling schemes for long-term retention of hyperpolarization. With such labeling schemes we achieve decay time constants of above 20 minutes enabling hour-long molecular tracking. We observe particularly long lifetimes at low magnetic fields of 1 T and below because of reduced relaxation from chemical shift anisotropy [2,4–5]. Therefore, low magnetic fields become attractive, not only because of their affordability, but because they enable metabolic tracking on biological timescales. We discuss sensitivity scaling as a function of magnetic field, and present first principle insights as well as experimental demonstrations showing significant gains for longer waiting times as we move to lower fields [2,6]. Figure 1 illustrates our nascent technology and its potential for hyperpolarized low-field molecular MRI.

Furthermore, SABRE-SHEATH is becoming more and more general, with the ability to hyperpolarize a much larger set of substrates than conventional SABRE [2]. Most recently, we have even hyperpolarized $^{15}N_2$ gas in the *ortho* state and the potentially very long-lived *para* state. This generalization is sparking renewed interest in SABRE-SHEATH for analytical purposes. In combination with ultrasensitive zero-field NMR, this leads towards miniaturized chemical analysis by NMR on the go. SABRE-SHEATH hyperpolarized zero-field NMR will be reviewed [7] and future perspectives will be discussed.

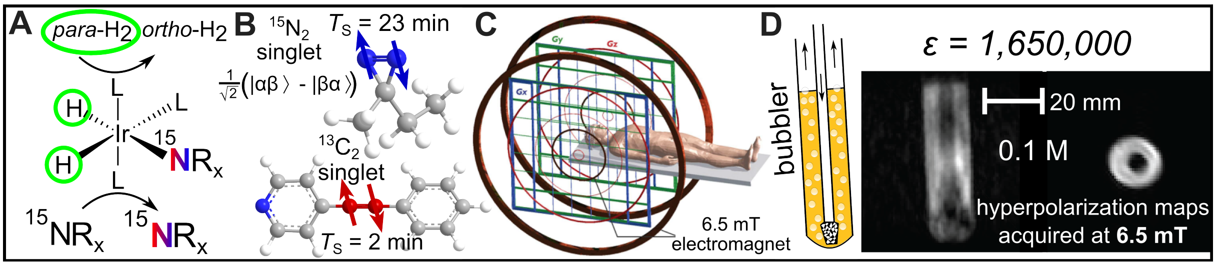

Figure 1: The combination of parahydrogen based hyperpolarization and low-field MRI. A) SABRE-SHEATH: parahydrogen is bubbled through a room-temperature solution in magnetic shields. At the established μT fields the polarization transfer catalyst pumps hyperpolarization from parahydrogen to a wide range of molecules with diverse R-groups. B) SABRE-SHEATH also hyperpolarizes long-lived singlet states, which enables hour-long tracking. C) Low-field electromagnet used for acquisition of low-field images [5]. D) Low-field ^{1}H images of a 0.1 M hyperpolarized solution of pyridine. The low-field signals are enhanced by more than one million fold.

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Ultra-sensitive detection of catalytic intermediates. The PANEL experiment

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The ^{1}H-NMR signal of dissolved molecular hydrogen enriched in parahydrogen (p-H_2) exhibits in the presence of an organometallic hydrogenation catalyst an unusual, partially negative line shape (PNL). It results from a strongly enhanced two-spin order connected to the population of the T_0 level of orthohydrogen (o-H_2). This two-spin order is made visible by a slow asymmetric exchange process between free hydrogen and a transient catalyst-hydrogen complex. By "only parahydrogen spectroscopy" (OPSY) it is possible to selectively detect the two-spin order and suppress the signal from the thermal o-H_2. The intensity of the PNL can be strongly affected by the "partially negative line" (PANEL) experiment [1], which irradiates a long narrow-band radio frequency (RF) pulse. When the RF is in resonance with the chemical shift values of the hydrogen bound to the elusive catalyst or of the free hydrogen, a strong intensity reduction of the PNL is observed. Numerical simulations of the experiments performed at 500 MHz and 700 MHz proton frequency show that the indirect detection has at least three orders of magnitude higher sensitivity than the normal NMR experiment. A theoretical model, including reversible binding and $S-T_0$ evolution, is developed, which reproduces the NMR lineshape, the nutation-angle dependence and the dependence on the frequency of the irradiation field of the PNL, and permits the determination of the proton chemical shift values and the sign of the scalar coupling in the transient NMR invisible complex where singlet-triplet conversion takes place.

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Parahydrogen induced polarization. Nanocatalysts and metabolites

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Parahydrogen induced polarization (PHIP) is a technique of hyperpolarization in nuclear magnetic resonance (NMR) for enhancing NMR signals over multiple orders of magnitude [1,2]. It utilizes the nuclear singlet state of parahydrogen, which upon addition to a molecule of interest (hydrogenation) is converted into observable magnetization [1,2]. The hyperpolarized molecules may then act as molecular imaging agents for diseases. Recent advances have made it possible to polarize metabolites, significantly broadening the spectrum of applications for PHIP [3]. The hydrogenation process typically requires a transition metal catalyst to effectively generate polarization on a short time scale to obtain high levels of polarization [1]. For *in vivo* experiments it would be desirable to remove the metal catalyst before injection to mitigate toxicity concerns and to allow for easy recycling of the catalyst. To achieve this, a heterogeneous catalyst that can be filtered before *in vivo* injection of hyperpolarized materials would be an elegant solution.

I will present heterogeneous nanocatalysts based on platinum and palladium that are capped with ligands and allow for maintaining the quantum correlation of parahydrogen to generate high levels of polarization [4—6]. The influence of the metal and the utilized ligands on the achieved hyperpolarization will be discussed. Finally, it will be shown that it is possible with palladium nanoparticles to hyperpolarize metabolites such as amino acids and acetate. The observed hyperpolarization for protons and ^{13}C exceeds 1%, bringing *in vivo* applications within reach [6].

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Hyperpolarized NMR contrast agents for molecular imaging

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The significant (usually orders-of-magnitude) increase in nuclear spin polarization above the thermal-equilibrium level is called hyperpolarization. Because the NMR signal is directly proportional to the nuclear spin polarization, the realized polarization enhancement manifests in the corresponding NMR signal and corresponding gains in detection sensitivity, which can be ≈ 6–8 orders of magnitude depending on the detection field of the MRI scanner [1]. Recent developments in NMR hyperpolarization have enabled a wide range of new *in vivo* molecular imaging modalities, ranging from functional imaging of the lungs to metabolic imaging of cancer. Our research explores selected advances in methods for the preparation and use of hyperpolarized contrast agents, some of which are already at or near the phase of their preclinical [2] and clinical validation [3]. Biomedical applications of hyperpolarized contrast agents require (i) high polarization level of relatively long-lived hyperpolarized molecules [3,4], (ii) preparation of pure hyperpolarized substrates [5] in (iii) biocompatible administration medium [6]. Preparation of such agents in the context of conventional parahydrogen induced polarization (PHIP) using molecular addition of parahydrogen and signal amplification by reversible exchange (SABRE) using reversible exchange of parahydrogen demands new advances in synthetic chemistry of contrast agents, *i.e.*, sophisticated isotopic enrichment and synthetic schemes, and advances in chemistry and spin physics of homogeneous and heterogeneous hydrogenation and exchange catalysis.

The significantly enhanced NMR hyperpolarization-endowed signal can enable high-quality clinical 3D images of hyperpolarized contrast agents to be obtained in as little as a few seconds. Moreover, because the hyperpolarized nuclear state is no longer endowed by the static magnetic field of the detecting NMR magnet, high-field MRI scanners are no longer mandatory, and lower-cost, less-confining, low-field 3D MRI can be used instead – with detection sensitivity potentially approaching or even surpassing that of high-field MRI.

This presentation will focus of our recent advances in (i) development of automated instrumentation for preparation of hyperpolarized contrast agents using parahydrogen and xenon-129 [3,7], (ii) developing new chemistries for preparation of hyperpolarized contrast agents to probe lung function using hyperpolarized proton MRI [8], elevated glycolysis in cancer [2,6,9], brain metabolism, and pH [10] and hypoxia imaging [11], and (iii) improving hyperpolarized MRI detection sensitivity by utilizing low-field MRI [12].

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Spin state dynamics in exciton fission and fusion

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Repackaging energy through downconversion (1 to 2) and/or upconversion (2 to 1) can boost solar energy conversion efficiencies by 30% or more. In organic semiconductors, the Frenkel character of the excitons leads to separate singlet and triplet bands, providing an ideal set of energy levels for both processes [1]. Singlet fission is a downconversion process in which a high-energy singlet exciton splits into a pair of triplet excitons via a spin-allowed transition. Over the last decade, we have made efforts to elucidate the basic photophysics of singlet fission using time-resolved transient absorption, photoluminescence and magnetic field effects [2–4]. While electronic coupling due to molecular packing geometries plays a key role controlling the fission rate [5], the importance of spin interactions in this process is only beginning to be examined in a systematic way. For singlet fission, nonequilibrium spin state distributions can play an important role in both the ultimate triplet yield and the observation of experimental quantities like delayed fluorescence. We will describe time-resolved experiments and Monte Carlo simulations that look at how spin dynamics affect both processes. The inverse of singlet fission is triplet–triplet annihilation, where two low energy triplet excitons fuse into a higher energy singlet. In this process, the triplet spin states on the organic molecules play an important role as well.

Spin states in sensitizers can also be important. For example, inorganic nanocrystal sensitizers show efficient energy transfer to molecular triplet states and enable the harvesting of low energy photons into the near-infrared region [6]. In these systems, the energy transfer may be enabled by isoenergetic triplet-like dark states of the nanocrystals. The dynamics of triplet states determine the efficiency of both fission and fusion dynamics, and thus their ultimate technological potential as mechanisms for energy downconversion and upconversion. Manipulating triplet spin states may be a promising approach for the optimization of both processes.

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Characterization of triplet pairs generated by singlet fission

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Singlet fission (SF) is a process in which a singlet exciton is converted to two triplet excitons in organic materials [1]. The two triplet excitons are coupled and the resultant triplet pair (TP) can take singlet, triplet and quintet spin states. SF is a spin conservative transition from the singlet exciton to a singlet TP and typically occurs on a ps or fs timescale. TPs have been recognized as important chemical intermediates in SF although TPs are unobservable intermediates in many cases due to their short lifetime.

In the past decade, there has been a renewed interest in the SF mechanism because SF has high potential to improve the efficiency of solar photovoltaics [1]. Recent time-resolved studies focused on the structure-function relationship of SF on the molecular level. Multiexciton states generated by SF were identified with ultrafast spectroscopy. Very recently TPs in a quintet state were detected by time-resolved EPR spectroscopy [2,3]. However the detailed structure of TP has not been reported.

In this contribution, we study magnetic field effects (MFEs) on the intensity of fluorescence from organic crystals and characterize structures of TPs generated by SF. MFEs on fluorescence have been observed in SF materials since the 1960s [4,5]. In addition to the known MFEs, we observed MFEs caused by the level crossing mechanism in high and low magnetic fields [6,7]. In the high magnetic fields, the observed MFE was generated in a correlated TP in which the two triplet excitons are coupled with the exchange interaction. In the low magnetic fields, the observed MFEs was associated with a separated TP in which the exchange interaction is negligible. In both cases, MFEs were generated with spin state mixing promoted by the highly anisotropic dipole-dipole interaction in a triplet exciton. Thus the observed MFEs contain detailed information on orientations of triplet pairs. Structure of TPs are discussed with the analysis of MFEs caused by level crossing mechanism.

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Zero quantum coherence in covalent spin-correlated radical pairs

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Photo-initiated sub-nanosecond electron transfer within covalently linked electron donor–acceptor molecules can result in the formation of a spin-correlated radical pair (SCRP) with a well-defined initial singlet spin configuration. Subsequent coherent mixing between the SCRP singlet and triplet $M_S = 0$ spin states, the so-called zero quantum coherence (ZQC), is of potential interest in quantum information processing applications because the ZQC can be probed using pulse electron paramagnetic resonance (pulse-EPR) techniques. Here, pulse-EPR spectroscopy is utilized to examine the ZQC oscillation frequencies and ZQC dephasing in structurally well-defined D–A systems. While transitions between the singlet and triplet $M_S = 0$ spin states are formally forbidden ($\Delta M_S = 0$), they can be addressed using specific microwave pulse turning angles to map information from the ZQC onto observable single quantum coherences. In addition, by using structural variations to tune the singlet–triplet energy gap, the ZQC frequencies determined for this series of molecules indicates a stronger dependence on the electronic g-factor than on electron-nuclear hyperfine interactions. We are also exploring the spin-forbidden double quantum coherences in order to obtain a full quantum tomography of this highly polarized two-spin system.

Recombination fluorescence as a way of probing the spin-correlated radical ion pairs created in polymeric systems by high-energy radiation

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It is of common knowledge that the Pauli exclusion principle together with the Coulomb interaction necessitate a coupling between energy and total electron spin of molecular states. This factor underlies a variety of external magnetic field effects (MFEs) on processes and phenomena, in which oppositely charged carriers of unpaired electrons, that are radical ions or polarons, can recombine with the formation of molecular products of a particular spin multiplicity. Among these phenomena is recombination fluorescence, by which it is possible to monitor the recombination process for those radical ion pairs (RIPs) that are in the singlet spin state at the moment of their recombination.

In this contribution, the recombination fluorescence generated in organic media by high-energy radiation is considered. In this case, recombining radical ions initially are typically singlet correlated and are separated by several nanometers. Therefore, this case is different from two other typical experimental situations, in which spin coherence effects of RIP recombination in organic media are investigated. These mentioned situations relate to studies of photoinduced charge separation in solutions and to conductivity measurements in amorphous solids.

As for the generation of spin-correlated RIPs using optical photons, the initial distance between the RIP's partners is typically rather short, < 1 nm. Thus, observing MFEs, which are formed due to singlet–triplet transitions, requires a comparatively low RIP recombination rate in parallel with sufficiently effective transformation of the starting RIP to so-called solvent separated pair to decrease exchange interaction. Ultimately, the range of radical ions as well as suitable solvents, which could be studied using this approach, is limited due to specific thermodynamic requirements for both the forward and reverse electron transfer. Besides, this suggests a non-trivial interplay between spin evolution and relative motion of the recombining RIP's partners.

As regards the conductivity measurements in non-ferromagnetic amorphous systems, charge carriers coming from different sides of a sample are not spin correlated at their first encounter. In this case, MFEs could be expected if RIP recombination probability was a spin-dependent process and the encounters were repeated. Again, these factors are expected to lead to some restrictions regarding both thermodynamics and kinetics of the processes involved.

The use of high-energy radiation offers, therefore, additional possibilities regarding the range of radical ionic or polaron states, which can be probed through spin coherence effects in organic media. In this work, the first experimental results, which were obtained on studies of MFEs in recombination fluorescence from irradiated conjugated polymers and their blends, are presented. Due to the unique experimental equipment providing high time resolution, the time-resolved MFE curves reveal details of spin dynamics in spin-correlated RIPs on a time scale of a few nanoseconds.

Magnetic field effects in organic semiconductors

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Organic semiconductors differ from inorganic crystalline electronic and optoelectronic materials such as silicon and gallium nitrides in that the underlying electronic and optical processes are highly localized, typically to the scale of a single or a few molecules. Intriguingly, the OLED display, as featured in millions of smartphones, is remarkably similar in its underlying operational principles to biological processes involving photoinduced electron transfer: electrically injected positive and negative carriers recombine to generate light. Since pure hydrocarbons are characterized by very weak spin-orbit coupling, spin is a good quantum number and carrier recombination in an OLED results in pure singlet and triplet excited-state species, of which only the former is dipole coupled to the ground state. This spin-dependent recombination in the solid state opens up a wide range of static and resonant magnetic field effects, which can be probed either in luminescence or current of the OLED, in principle down to the level of single photons or electrons. Many interesting analogies of these solid-state processes exist to radical-pair-based mechanisms in solutions.

This presentation aims to provide a brief overview of the range of magnetic field effects observed in organic semiconductors while touching on thematic connections to fields as diverse as STM-based single-molecule transport spectroscopy, spin chemistry and the possibility of spin injection. In OLEDs, magnetic field sensitivity on the nT scale was recently reported [1]. Because singlet and triplet spin pairs recombine as singlet and triplet excitons, the radical-pair mechanism can be probed by the interconversion between fluorescing and phosphorescing species, a phenomenon which is perturbed under continuous-wave magnetic resonance [2]. Pulsed magnetic resonance allows the direct visualization of spin-Rabi flopping in the device current, a process, which can occur both on the single spin or in the spin pair with doubled precession frequency [3]. Spin coherence can be probed at room temperature by spin-echo spectroscopy, a method so sensitive to even allow the perturbation of the device current by NMR [4]. Although many of the effects observed in organic semiconductors are basically monomolecular in nature, the high material density along with the ability to design a range of device geometries means that more exotic parameter regimes can be probed, which are hard to access in conventional magnetospectroscopy. Examples include the regime of ultrastrong resonant driving, where the Rabi frequency exceeds the transition frequency of the Zeeman-split spin levels [5,6], and the spin-Hall effect.

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Photoconductivity and magnetoconductance effect on vacuum vapor deposition films of weak charge-transfer complexes

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Organic electronic materials have attracted considerable academic and industrial research interest for over the past decades as a potential candidate for next-generation of technology. Thin films of organic semiconductors are successfully used in organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic solar cells (OSCs). The magnetoconductance (MC) effect is a characteristic property arising from the electron's spin degree of freedom and the diffusion of spin carrier. MC effects on current and emission in the organic thin-film devices, such as OLEDs, OSCs, and so on, have been received considerable attention during the last decade. In this work, we have prepared thin films of weak charge-transfer (CT) complexes (pyrene/dimethylpyromellitdiimide, Py/DMPI or pyrene/pyromellitic dianhydride, Py/PMDA) on an interdigitated platinum electrode by vacuum vapor deposition. Their photoconductivity and MC effect on the photocurrent were investigated as shown in Figure 1(a) and 1(b), respectively. Mobile triplet excitons (probably CT excitons) were detected by single-crystal time-resolved ESR (TRESR) experiments at room temperature. A successful simulation of the MC effect was achieved by quantum-mechanical simulation assuming two types of collision mechanisms between the spin-doublet electron and hole carriers (DD pair mechanism) and between the trapped triplet excitons and mobile doublet carriers (TD pair mechanism), when the parameters (g, D, E, and polarization) determined by TRESR and the effective hyperfine splitting estimated from an *ab initio* molecular-orbital calculation were used [1].

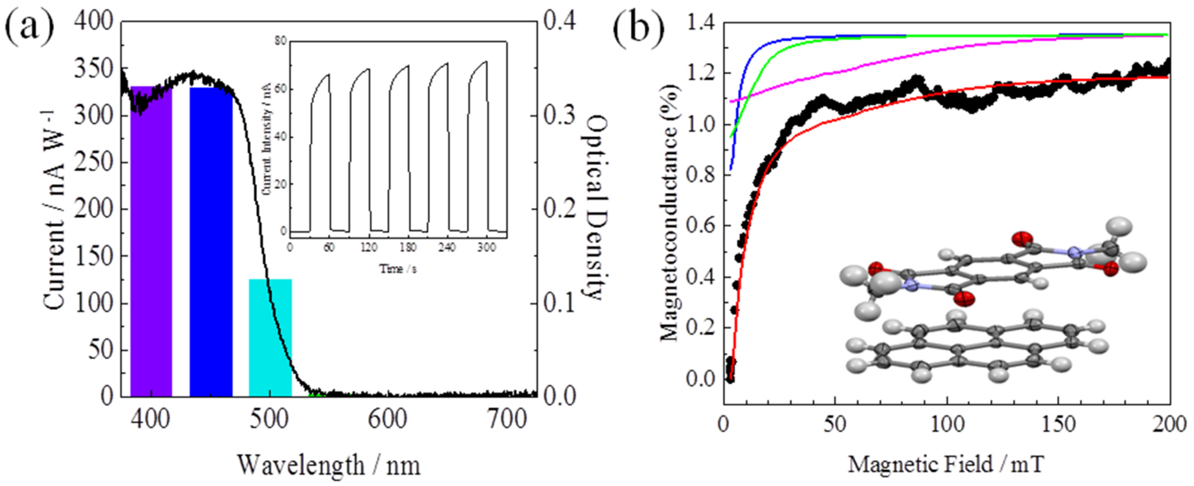

Figure 1: Photocurrent response and MC effect of Py/DMPI VVD film. (a) Wavelength dependence of the photocurrent and current response for the ON/OFF cycles of light irradiation. (b) MC effects in the photocurrent. The blue solid curve was obtained by the spin-doublet electron-hole pair (DD) mechanism and the green and purple curves were simulated by the triplet-doublet (TD) mechanism.

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Conversion of singlet spin state of pair of radicals coupled with exchange or dipole-dipole interaction into non-zero total spin hyperpolarization by means of adiabatic switching of strong microwave field

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Recently, a new method has been proposed allowing one to convert initial multiplet nuclear spin order into polarization of almost any desired kind [1-2]. It is based on hyperpolarizing a system of scalar coupled nuclear spins in the presence of a strong RF-field, which is subsequently slowly (adiabatically) reduced to zero. The method allows one to convert multiplet polarization into net hyperpolarization without any loss. The correct choice of the frequency of the RF field makes it possible to change the sign of the integral polarization.

In this study, we theoretically check the possibility to extend this approach also for conversion of initial multiplet electron spin order into net electron polarization. The system under study is a radical pair with spins of radicals coupled by dipole–dipole or exchange interaction which initially is formed in singlet spin state in the presence of a strong MW-field, which is subsequently slowly (adiabatically) reduced to zero. Such the system can serve photo-induced charge-separated radical pair in photovoltaic cells and radicals in solution linked by rigid molecular bridge. The spectrum resulting from adiabatic switching of the strong MW field will be analyzed with taking into account of orientation averaging in case when electron spins are coupled by dipole–dipole interaction. The effect of setting the MW-field frequency will be investigated.

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T49

Charge separation and recombination in triads based on dipyrrin complexes of iridium, palladium and platinum

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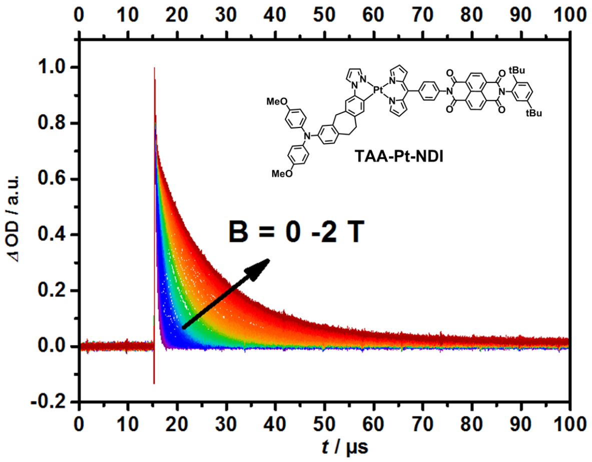
Photoinduced electron transfer, the primary step in photosynthesis, was studied in a series of donor–iridium(dipyrrin)–acceptor triads as novel model compounds. They show long-lived (ca. 500 ns in MeCN) charge-separated (CS) states with very high quantum yields [1,2]. The charge recombination kinetics exhibit strong magnetic field dependences with lifetime prolongation of the CS state by a factor 4−7. At fields >10 mT the decay becomes biexponential. The magnetic field effects (MFEs) are a clear indication of spin processes becoming rate determining. The magnetic field dependent kinetics is well described by the Hayashi-Nagakura scheme, which turned out to provide a good phenomonological basis not only for the high-field regime where relaxation processes dominate, as originally conceived by Hayashi and Nagakura, but also in the low-field regime where coherent hyperfine-coupling-driven processes dominate. Surprisingly, the two regimes are clearly reflected by two steps in the field dependence of an effective rate constant of spin relaxation.

Replacing the iridium by platinum leads to a TAA–Pt–NDI triad, which shows a much prolonged lifetime of the charge separated state. This indicates that the electronic coupling is strongly influenced by the central metal atom. Again, a strong MFE was observed which extends into much higher fields than in case of the iridium triad.

Replacing the central metal complex by a phenyl unit leads to the occurrence of pronounced level crossing effects in the field-dependent charge-recombination kinetics, from which exchange interactions on the order of 10−20 mT can be quantitatively evaluated. They show a systematic dependence on the nature of substituents at the central phenyl ring.



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Global energy functions for spin processes in radical pairs

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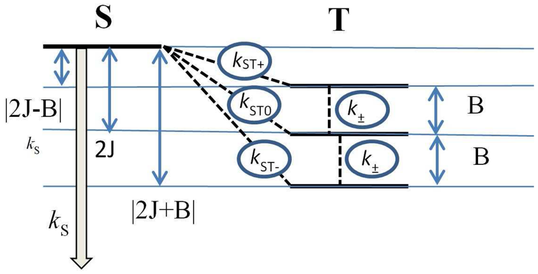
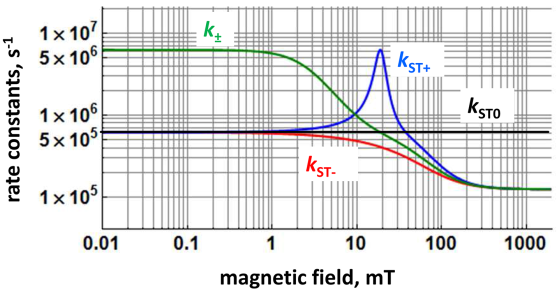
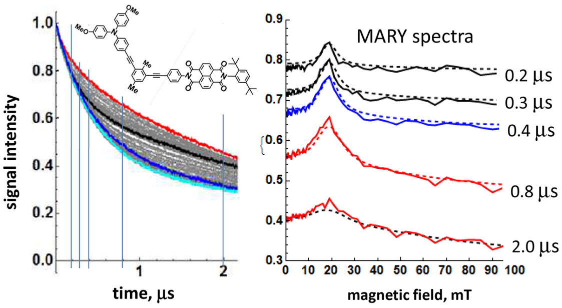
In this contribution, a theoretical analysis of the magnetic field dependent charge recombination kinetics in the electron donor–acceptor systems D–X–A presented by C. Lambert will be provided. The charge-separated states of these compounds represent exemplary radical pairs in that both, coherent and incoherent spin processes underlying the kinetic magnetic field effect can be well simulated in a phenomenological way by a classical kinetic scheme [1,2] and show up as clearly distinct steps in the magnetic field dependence of an effective rate constant of spin conversion.





The quasi classical simulation is also applicable to the X = bisethynylphenyl bridged systems showing appreciable exchange interaction with $2J$ values of 20–30 mT. Whereas for systems with negligible J, spin processes connect only states with $\Delta E \asymp B$ or 0, the energy gaps for the rate constants k_{ST_+}, k_{ST_0}, k_{ST_-} and $k_\pm$ are all different (top Figure). It is shown that one global energy dependence $k(\Delta E)$ suffices to describe all of them (middle Figure). Examples of the experimental and simulated time-dependent MARY spectra are shown in the lower Figure.



The classical treatment was backed up by a full quantum dynamical treatment unifying coherent and incoherent spin dynamics in one stochastic Liouville equation [3].

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The role of level anti-crossings in nuclear spin hyperpolarization

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Spin hyperpolarization is a rapidly growing field in modern NMR. Current problems in spin hyperpolarization are dealing with optimizing polarization formation, as well as polarization transfer from primarily polarized spins to target nuclei of choice. Formation of polarization generated in the course of a chemical reaction, such as chemically induced dynamic nuclear polarization (CIDNP), optical nuclear polarization (ONP), parahydrogen induced polarization (PHIP), and the related signal amplification by reversible exchange (SABRE), if often optimal at specific strengths of the external magnetic fields: in the field dependence of polarization pronounced features are observed.

In this work, we propose to look at formation of polarization generated by different mechanisms from a common perspective. Specifically, we suggest assigning features in the field dependence of CIDNP, ONP and PHIP/SABRE to level crossings (LCs) and level anti-crossings (LACs) of reaction intermediates. Such an approach allows one to formulate a common theoretical description of liquid-state and solid-state CIDNP and to ease consideration of CIDNP in solids [1]. In the SABRE case such an LAC-based approach allows one to explain the field dependence of polarization in a simple and general way.

In hyperpolarization experiments, it is often desirable to transfer the initial spin order to other nuclei of choice, either to protons or to “insensitive” NMR nuclei, such as ^{13}C and ^{15}N. This situation arises primarily in CIDNP, PHIP and SABRE. In all cases it is desirable to perform such a polarization transfer at a high field of an NMR spectrometer to avoid demanding field-cycling. This can be achieved [2] when LAC conditions are generated by applying spin-locking RF-fields of appropriate strengths. Here, an analysis of polarization transfer in terms of LACs in the rotating frame is very useful to predict which spin orders are transferred depending on the strength and frequency of the B_1 field.

This work was supported by the Russian Foundation for Basic Research (project 17-03-00932) and the Russian Science Foundation (projects 14-13-01053 and 15-03-20035).

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Effects of very low magnetic fields on nuclear hyperpolarization

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Spin hyperpolarization is one of the characteristic attributes of spin chemistry and has been widely used for decades to analyze reaction processes and their pathways, to characterize reaction intermediates or just to boost the spectroscopic sensitivity of elusive species. Depending on the reaction type, hyperpolarization relies on different mechanisms, but they all have in common that their efficiency varies with the external magnetic field strength. Hence, variation of the field is a versatile tool for exploiting and manipulating the hyperpolarization process that usually includes transfer of spin order from an easily polarizable primary spin ensemble to the target spins of choice. Characteristic features in the field dependence are often related to avoided crossings (LACs) [1] of the spin levels, the position of which can be used to determine magnetic interactions parameters. For liquids, when the leading coupling term is scalar *J*-coupling, the LAC regime can go up to several Tesla for homonuclear spin groups. In contrast, for hetero-nuclei with their large difference in Larmor frequency, one has to reduce the field to 10^{-4} T or lower to find LACs.

This consideration gave the motivation for devising a field-cycling set-up that covers the full range between 10^{-8} T and 9.4 T. It is based on a digitally controlled shuttling system that moves the sample between the spectrometer magnet providing high resolution spectra in combination with a shielding permalloy barrel equipped with an ancillary set of coils for shimming and field control.

As an example, the polarization transfer between parahydrogen and ^{15}N or ^{13}C in SABRE (signal amplification by reversible exchange) experiments [2] is discussed that strongly varies in the range down to 10^{-8} T. Features of avoided level crossings (LACs) are clearly resolved and are used to characterize transient catalytic complexes.

Since hyperpolarization is of transient nature, it must be utilized before it returns to the equilibrium value driven by spin-lattice relaxation. Thus, for optimum use, information on the relaxation behavior and its field dependence (relaxation dispersion) is important. Of particular interest in this context are long-lived spin states, *i.e.*, spin configurations that are immune to major relaxation mechanisms. Prominent examples are singlet states. In this context, the strong influence of homo- and heteronuclear spin–spin coupling on the relaxation dispersion of biomolecules is demonstrated on the examples of adenosine monophosphate and methyl propiolate.

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Level anti-crossing concept and analysis of CIDNP and ONP in solids

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Nuclear spin hyperpolarization is often used for enhancing weak NMR signals. There are several hyperpolarization methods known, such as dynamical nuclear polarization (DNP), chemically induced dynamic nuclear polarization (CIDNP), optical nuclear polarization (ONP), and parahydrogen induced polarization (PHIP). Presently, there is a growing interest to spin hyperpolarization in the solid state, because many chemical and biochemical processes take place in the solid state. As far as the theoretical treatment of hyperpolarization in solids is concerned, the main problem is the presence of anisotropic interactions rendering the spin dynamics very complex. While the mechanisms of polarization formation in liquids are well established and understood, detailed analyses of solid-state polarization mechanisms still remain challenging.

Recently we have shown that a theoretical approach based on level crossings (LC) and level anti-crossings (LAC) is an efficient tool to reveal the complex spin dynamics in the case of CIDNP. In solids, all features in the field dependence of CIDNP come from the LACs, because anisotropic interactions result in perturbations, which turn LCs into LACs. We have interpreted known CIDNP mechanisms in terms of the LAC concept. This consideration allows one to find analytical expressions for the magnetic field range, where different CIDNP mechanisms are operative; furthermore, the LAC description gives a clear way to determine CIDNP sign rules. We also propose to analyze triplet-state ONP in molecular crystals in terms of level crossing phenomena as well, namely, to attribute features in the ONP magnetic field dependence to LACs in a radical pair. Like in the CIDNP case, anisotropic interactions play a significant role in ONP formation. Using this method, we have analyzed the orientation dependence of ONP and derived analytical formulas for the positions of LAC-derived features in the field dependence of polarization. Kinetics of ONP in the presence of microwave irradiation was also analyzed using the “fictitious spin” description of the electronic triplet state.

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Electron spin polarization in natural and artificial photosynthesis

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The photosynthetic conversion of solar energy by light-induced energy and electron transfer generates a series of sequential radical pairs and in some cases excited triplet states. Because of the time scales involved these species exhibit electron spin polarization and coherent oscillations. An overview of how these effects have been used to characterize the natural photosystems will be presented with emphasis on recent results in type I photosynthetic reaction centers. These protein complexes are made up of two core proteins that form a dimer and in some case there are a number of additional peripheral proteins. In contrast to type II RCs in which the electron transfer is unidirectional, in type I RCs it occurs along two branches of cofactors associated with the two proteins of the dimer. The nature of the initial charge separation is still a point of debate but some of the proposed models raise the intriguing possibility that a coherent superposition of the charge-separated states could exist. In heliobacteria, the reaction center is composed of two identical protein subunits and the primary donor in the electron transfer is a special pair of bacteriochlorophyll (BChl) g' molecules referred to as P_{800}. It is known that in presence of light and oxygen BChl g is converted to Chl a_F and the RC ceases to function [1].

However, our recent EPR, ENDOR and optical data indicate that the loss of function is not linear in the conversion of the BChl g and that partial oxidation of the complex leads to formation of a BChl g'/Chl a_F' special pair that is functionally active and breaks the symmetry of the complex. This finding suggests that the change in symmetry and probable loss of electron transfer in one branch does not impede the function of the reaction center significantly. Artificial mimics of the natural systems have been widely studied and some recent examples will also be presented. In the natural photosystems, electron transfer occurs exclusively from the excited singlet state of the donor. However, we have recently shown [2] that triplet electron transfer can be promoted by introduction of a heavy metal in the donor. This results in a lower driving force for electron transfer but a higher overall yield because the longer lifetime of the excited triplet state allows for slower forward rates.

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Electron spin polarization imaging of photoinduced primary charge-separated states in PSII

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In the primary event of photosynthesis by green plants and cyanobacteria, the light energy is transferred through antenna complexes to the reaction center (RC) of the photosystem II (PSII) in the thylakoid membrane. The RC is composed of the D1/D2 heterodimer, possessing the chlorophyll *a* (Chl*a*) pair (P_{D1}/P_{D2}), the accessory Chl*a* (Chl_{D1}/Chl_{D2}), the pheophytins ($Pheo_{D1}/Pheo_{D2}$), two quinones, and two additional Chl*a* molecules as the redox active cofactors. It has been suggested that the electron is transferred to $Pheo_{D1}$ from ${}^1Chl^*_{D1}$ electronically excited *via* the antenna, following hole-transfer to the "special pair (P)" of P_{D1}/P_{D2} generating the primary charge-separated (CS) state of $P^{+\bullet}\,Pheo^{-\bullet}_{D1}$. Several studies have been performed to understand mechanisms of an extremely high redox potential of $P^{+\bullet}$ in PSII while the photosynthetic reaction centers (PRC) do not have such potentials in purple bacteria. For chemically oxidized PSII RC samples, the cationic charge is known to be localized on the D1 part (P_{D1}) at 70−80% over P_{D1}/P_{D2}, lowering the singly occupied molecular orbital (SOMO) level to oxidize the Mn_4CaO_5 cluster. On the primary CS state, Matysik *et al.* demonstrated that the cationic charge is localized at a single Chl*a* site by using the photo-CIDNP method [1].

In the primary CS states, the above oxidative and localized cationic charge would cause a strong electronic interaction in $P^{+\bullet}_{D1}\,Pheo^{-\bullet}_{D1}$ and thus suffer from an energy-wasting charge recombination (CR) process, since the distance (1.5 nm) between $P^{+\bullet}_{D1}$ and $Pheo^{-\bullet}_{D1}$ is expected to be shorter than the CS distance of 1.8 nm in *Rhodobacter sphaeroides* [2] in which the hole distribution is highly delocalized on the special pair. However, a lifetime (τ) of 200 ns was obtained for the primary CS state in the quinone doubly-reduced membrane of PSII, while $\tau = 25$ ns is significantly shorter in *Rhodobacter sphaeroides*. On this, no experimental studies have been performed to understand how cofactor geometries play roles on the electronic interaction of the primary CS state in which the anionic charge may significantly influence the electronic state.

We have observed the primary CS states in quinone pre-reduced membranes of PSII from spinach in frozen solution and in oriented multilayers at 77 K using an X-band time-resolved EPR (TREPR) method. Herein, we propose a novel method of "3D spin polarization imaging", by which the anisotropic spin polarization is mapped to all possible magnetic field directions from the powder-pattern TREPR to obtain geometries of the primary CS state [3]. We also show that the electronic coupling between the charges is significantly weak although the tunneling route is geometrically active after the primary charge separations [3].

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Abstracts of Posters

Magnetic field effects on luminescence in multichromophoric metalloporphyrin-based systems

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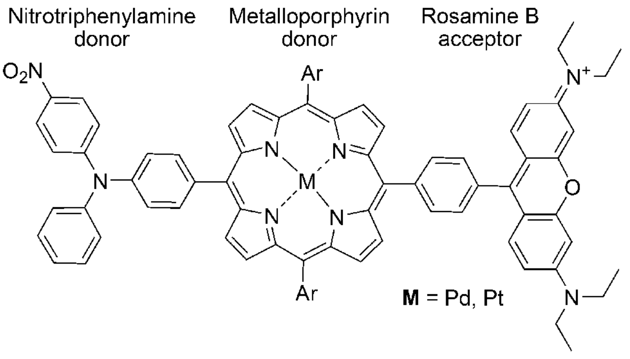
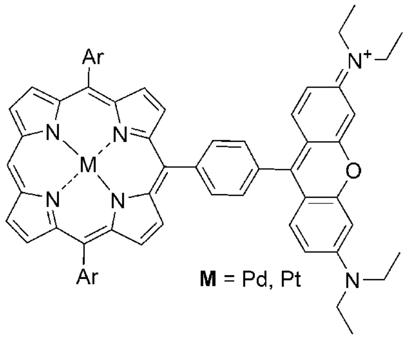
We report experiments exploring MFEs on luminescence in a series of dyads and triads comprising Pt or Pd porphyrins covalently bound to rosamine B (RosB, acceptor) and nitrotriphenylamine (donor) chromophores. Upon photoexcitation, the above systems undergo electron transfer, generating radical pairs (RPs), whose energies are higher than those of the local metalloporphyrin triplet states. Since Pt and Pd porphyrins are highly phosphorescent (including in solutions at ambient temperatures), MFEs on the spin dynamics in the RPs may be monitored by the phosphorescence [1]. The MFEs are expected to be different depending on the initial state of the RP and thus on the initially excited chromophore: RosB *versus* metalloporphyrin.

Indeed, in some of the studied systems, MFEs on the phosphorescence were observed, although generally of low magnitude. Similar to the previously reported Pt porphyrin–RosB dyads [2], MFEs were detected even when the initially populated state of the system was the locally excited triplet state of the metalloporphyrin, suggesting that the RP was generated by endergonic electron transfer.

Remarkably, in some of the studied systems we observed long-lived emission (ca. 100 μs) spectroscopically identical to the fluorescence of RosB, *i.e.*, delayed RosB fluorescence. Although the local triplet state of RosB could be populated via, *e.g.*, triplet–triplet energy transfer from the triplet state of the metalloporphyrin, extremely weak spin–orbit coupling and the large S–T gap in RosB make thermal population of its singlet state highly unlikely. One possible mechanism involves participation of RP intermediates, which connect the metalloporphyrin triplet and RosB singlet states.





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Magnetosensitive flavin photochemistry in micron-scale reaction environments

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The magnetosensitivity of photochemical reactions is of relevance across diverse disciplines from solid-state photonic devices to animal navigation. The latter, animal navigation, involves numerous species that are known to use the geomagnetic field for orientation and navigation, termed magnetoreception. The mechanism by which this magnetoreception works is still under debate. One hypothesis, chemical magnetoreception, involves the radical pair mechanism (RPM), in which magnetic fields can influence the rate and yield of chemical reactions. The proposed receptor molecule in this hypothesis is the blue-light receptor protein, cryptochrome [1]. Cryptochrome photochemistry involves photoinduced intermolecular electron transfer reactions, which produce radical pairs comprising of a reduced flavin cofactor and an oxidized tryptophan residue inside the protein [2].

Scientists from different fields, ranging from spin chemists to behavioural biologists, have conducted much research in an attempt to unravel this mystery, but still an experiment is needed to establish that cryptochrome actually is the magnetoreceptor in living cells. To this end, we proposed a spatially resolved spectroscopic approach. This has led us to develop both transient optical absorption detection (TOAD) and magnetically intensity modulation (MIM) imaging microscopies [3].

Immobilisation of flavins is desirable to simulate the orientationally structured protein environment of cryptochrome. In this work, we study the photochemistry and magnetosensitivity of flavins in a range of different local microenvironments, for example, starch films and vesicles. Initial experiments on DOPC giant unilamellar vesicles (GUVs) display the capabilities of the TOAD technique. Flavin mononucleotide (FMN) and hen egg-white lysozyme (HEWL) were encapsulated within DOPC GUVs (diameter 10–30 μm). Results show a TOAD image of flavin excited triplet state and semiquinone radicals, which according to photo-CIDNP studies [4], are generated by electron-transfer reaction from the exposed aromatic tryptophan residues (Trp-62 and Trp-123) in the native state of HEWL. These initial results display that TOAD imaging has the potential to observe flavin radicals inside living cells.

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Observation of spin polarization in the charge transfer excited state of copper(I) complexes by time-resolved EPR spectroscopy

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Copper(I) complexes which exhibit visible emission attract considerable attention due to their potential application to OLEDs, sensors and photosensitizers for photo-energy conversion processes. Although bisphenanthroline copper(I) compounds are rather unstable in the excited state, heteroleptic copper(I) complexes bearing phenanthroline and diphosphine ligands show intense emission principally from the lowest excited triplet metal-to-ligand charge transfer state with rather a longer lifetime, and thus are one of the most promising candidates for redox-photosensitizers. Therefore, in this kind of heteroleptic copper(I) complexes, various attempts have been made to prolong lifetimes further and to stabilize the charge transfer excited state as a precursor of photo redox reactions. However, lack of detailed information on the electronic structure of the charge transfer excited state involving a transition metal ion, prevents us from efficient design and development of new compounds having much better functionalities.

Time-resolved EPR is a powerful tool to know not only spin distribution but also fine structure of excited triplet states. Since charge transfer excited states of transition metal complexes, such as Ru(II) and Os(II) compounds, have large zero-field splittings, *e.g.*, more than 10 cm^{-1}, it has not been feasible to detect their excited state by time-resolved EPR. On the other hand, copper is a first-row transition metal, and its spin-orbit coupling is expected not to be as large as those of transition metals of the second and third row. We have succeeded to observe spin-polarization of the excited triplet state in a couple of copper(I) complexes bearing phenanthroline and diphosphine ligands at lower temperature by using X- and Q-band time-resolved EPR. In the X-band EPR spectra, only broad emissive features were observed mainly in the lower magnetic-field region. On the other hand, in the Q-band EPR spectra, spin-polarized signals were observed in a wide range of the magnetic field. Large D values ($\approx 1\ \mathrm{cm}^{-1}$) were suggested based on spectral simulations. The structures of the charge transfer excited triplet states as well as excited-state dynamics will be discussed, in particular, concerning the role of diphosphine ligands.

Hyperpolarization of an AA'X spin system. Surviving para-order and decoupling effects

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Motivation. Magnetic resonance imaging (MRI) is a widely used technique in clinical diagnosis; however, it suffers from low sensitivity. The hyperpolarization of nuclear spins promises to overcome the low thermal polarization of MRI, paving the way for new applications. The "PASADENA" approach [1] makes use of the spin order of parahydrogen (p-H_2), which is added to a precursor molecule to increase the signal. Various spin-order transfer sequences were developed to convert the available spin order into magnetization of a third spin-$\frac{1}{2}$ nucleus to suit the properties of the newly formed spin system. The PH-INEPT+ sequence [2] (PS) was designed to convert double spin order into magnetization, whereas Goldman's sequence [3] (GS) was designed for singlet order. The kind of spin order that is available after hydrogenation depends on the Hamiltonian of the system (AA'X, ABX), whose J-couplings can be suppressed by decoupling. Here, we investigate the effect of decoupling on an AA'X spin system (succinate) and subsequent hyperpolarization by PS and GS.

Methods. 1-^{13}C, 2,3-$^{2}H_2$-succinate, an AA'X system, was formed by catalytic parahydrogenation of fumarate, and hyperpolarization by SAMBADENA [4] directly in the bore of a 7-T MRI (Biospec 7/20, PV 5.1, Bruker, Germany). PS, or GS with and without ^{1}H-decoupling, were played out 5 s after the onset of the p-H_2-injection. Simulations were carried out to predict polarization and to optimize the intervals of PS and GS. The effect of decoupling during the hydrogenation was approximated by calculating a time-averaged density matrix, and relaxation was neglected.

Results. For GS with and without continuous-wave decoupling, a ^{13}C-hyperpolarization $\approx$ 8% (theory: 99%) and 2% (55%) was achieved, respectively. For PS without decoupling, $\approx$ 0.5% (21%) was achieved.

Discussion. In all cases, significant hyperpolarization was observed. This indicates that transferable spin order survived the hydrogenation and relaxation, and that succinate satisfies the requirements for both sequences. Furthermore, decoupling appears to further reduce the loss of spin order, as the GS hyperpolarization was increased when decoupling was applied. The same but less pronounced effect was observed in simulations. Note, that a new sequence was reported [5], yielding experimental hyperpolarization $\approx$ 9% for an near-equivalent system like succinate.

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Solid-state photo-CIDNP allows for observation of protons in photosynthetic cofactors in their native protein environment

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The origin of an extremely efficient electron transfer in the heart of natural photosynthetic complexes occurring during photosynthesis is still a mystery to be solved. Clear understanding of this phenomenon would allow for the construction of effective artificial photosynthetic systems. Despite the fact that the key players in the chain of the events during photosynthesis are known for most of the photosynthetic organisms, the origin of their unique properties is puzzling. One of the amazing features of photosynthetic reaction centers is the occurrence of the photochemically induced dynamic nuclear polarization (photo-CIDNP) effect. Since its discovery in 1994 by Zysmilich and McDermott [1] it has been developed into an analytical tool for studying the electronic structures of small photosynthetic cofactors embedded in huge protein membrane complexes, since it provides dramatic nuclear spin order that can be observed as strong signal enhancement (by the factor of 10,000–80,000 for ^{13}C) by magic angle spinning (MAS) NMR experiments [2,3]. Thus, successful combination of signal enhancement from selectively and strongly hyperpolarized ^{13}C nuclei with homonuclear ^{13}C–^{13}C correlation MAS NMR experiments allowed for studying electron donor and acceptor in the bacterial reaction center of *Rhodobacter* (*R.*) *sphaeroides*, revealing molecular electronic structures of the cofactors forming the primary radical pair in the electronic ground state [4], the charge-separated state [5], as well as the molecular triplet state [6]. Despite the successful observation of the the solid-state photo-CIDNP effect for ^{13}C and ^{15}N nuclei, MAS NMR experiments on ^{1}H failed to show the effect, thus hindering the insights into important details about hydrogen-bonding network around photosynthetic cofactors, the charge state of surrounding amino acids, etc.

In the present study, we explore the possibility to transfer the photo-CIDNP enhanced polarization from ^{13}C nuclei to nearby protons to be implemented in ^{13}C–^{1}H heteronuclear correlation experiments. As a first example, applicability of these new experiments was tested on the selectively ^{13}C-labeled reaction center of *R. sphaeroides* WT. Being a large membrane protein complex, this system is very challenging from the ^{1}H MAS NMR point of view. We expect that these types of experiments can open the access for studying the properties of protons of photosynthetic cofactors and surrounding amino acids in their native protein environment and allow for better understanding the role of the proton pool around the electron donor in the electron-transfer process.

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The path to enlightenment: What TREPR teaches us about electronic structure, morphology, and flexibility of conjugated polymers

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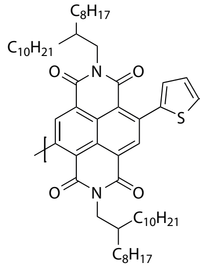
Illuminating conjugated polymers not only leads to excited states, but sheds light on some of the most important aspects of device efficiency in organic electronics as well. The interplay between electronic structure, morphology, flexibility, and local ordering, while at the heart of structure-function relationship of organic electronic materials, is still barely understood. Time-resolved EPR (TREPR) spectroscopy has proven valuable to gain further insight.

Previously, we established TREPR for probing both the orientation and degree of ordering of polymers [1], nicely complementing other methods for structure determination. In another study, we revealed the origin of triplet states, bringing a seemingly forgotten route back into focus: spin-forbidden direct $S_0 \rightarrow T$ excitation, with potential high impact for device efficiency [2].

Here, we demonstrate the power of TREPR, combined with DFT calculations, to discriminate between electronic structure and planarity when it comes to determining factors for exciton delocalisation. In a systematic approach, a series of building blocks of PNDIT2 as well as the polymer with two chain lengths have been studied. Surprisingly, the triplet exciton on PNDIT2 is highly localized, spanning no more than two repeat units, rendering the building block NDI–T2–NDI a perfect model for the polymer [3].



The polymer PNDIT2, consisting of naphthalenediimide (NDI) substituted with bithiophene (T2).

Additionally, we show the intrinsically high sensitivity of TREPR to the local environment of the exciton to make it an excellent tool for investigating polymer morphology. The parameters readily available from spectral simulations allow us to probe the available conformational subspace of the polymer backbone and thus the degree of order even in solution. PNDIT2 shows striking differences in different solvents, 1-chloronaphthalene and toluene, that can be attributed to the formation of locally highly ordered domains if dissolved in toluene. Additionally, different modes of exciton delocalisation, namely intra- and interchain, dominate depending on the solvent, the latter resembling the situation in thin film [4].

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[4] D.L. Meyer, R. Matsidik, S. Huettner, M. Sommer and T. Biskup, *submitted.*

Direct $S_0 \rightarrow T$ excitation of a conjugated polymer repeat unit: Unusual spin-forbidden transitions probed by TREPR spectroscopy

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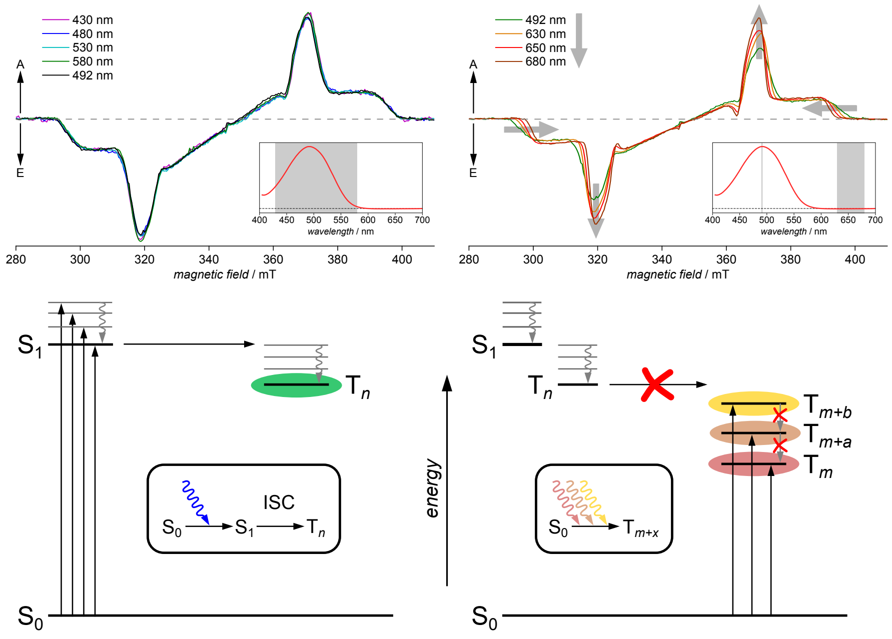
A detailed understanding of the electronic structure of semiconducting polymers and their building blocks is essential to develop efficient materials for organic electronics. (Time-resolved) electron paramagnetic resonance (EPR) is particularly suited to address these questions, allowing one to directly detect paramagnetic states and to reveal their spin-multiplicity, besides its clearly superior resolution compared to optical methods.



Summary of the results obtained via TREPR of triplet excitons pointing towards a direct $S_0 \rightarrow T$ excitation. Triplet spectra are observed if the molecule is excited far red from its optical absorption. Additionally, the triplet states originating from the red-shifted excitation exhibit clearly distinct spectral shapes. For details see [1].

We present here evidence for a direct $S_0 \rightarrow T$ optical excitation of distinct triplet states in the repeat unit of a conjugated polymer used in organic photovoltaics [1]. These states differ in their electronic structure from those populated via intersystem crossing from excited singlet states. This is an additional and so far unconsidered route to triplet states with potentially high impact on efficiency of organic electronic devices.

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EPR study of spin-dependent charge-transfer processes at electrodes

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We want to look for a spin dependence in the charge transfer that occurs at the interface between an electrode and an electrolyte. Chazalviel found evidence for spin dependence in the kinetics of the methyl viologen (MV) redox processes [1]. However, magneto-hydrodynamic effects may have played a role since he used a very large field range, from -2.5 to $+2.5$ T [2]. We want to use electrically detected electron paramagnetic resonance (ED-EPR) to detect a spin effect without changing the field significantly.

We developed an oxygen-tight electrochemical cell with a GaAs working electrode (WE), a silver wire reference electrode (RE) and a platinum wire counter electrode (CE), in a geometry compatible with EPR measurements. Cyclic voltammograms (CV) around the two reduction potentials of MV were performed. We developed a system for simultaneous standard continuous-wave EPR (9.8 GHz) and ED-EPR measurements. For various fields around the resonance condition, we measured the cell current while scanning the WE potential through both MV reduction peaks. We spin-polarized the p-doped GaAs cathode by optical spin pumping and used lock-in detection to monitor the modulation of the cell current due to field and light polarization modulation.

$MV^{\bullet +}$ radicals were produced either electrochemically *ex situ* or *in situ* with a Pt wire as sacrificial working electrode (WE2). We observed microwave radiation induced CV shifts, which decay slowly when light is shone on the electrode.

We are looking into other possible spin-polarization methods, such as chirality induced spin selectivity (CISS) [3].

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Magnetic field effects on cryptochromes and related model systems

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The ability of birds to orient themselves during migration using the Earth's magnetic field is hypothesized to involve cryptochrome proteins located in their retinae. Photochemical radical pair reactions within these proteins have product yields that are sensitive to the magnitude and direction of the external magnetic field, and have been proposed as the starting point for a more complex signalling cascade that allows birds to visualize the Earth's magnetic field. Cryptochromes are currently the only candidate magnetoreceptor for a biological, chemical compass based on the radical pair mechanism (RPM), but the relationship between the photochemistry and signal transduction in these proteins is largely unexplored. The work presented here involves a combination of fluorescence spectroscopy and hydrogen-deuterium exchange (HDX) experiments to investigate the photochemistry and photosignaling mechanisms, respectively, occurring in cryptochrome.

Fluorescence spectroscopy provides significant sensitivity gains over the traditional absorption-based techniques and has been used to study magnetic field effects (MFEs) in a variety of chemical systems related to cryptochrome to increase our understanding of the fundamental photophysics [1]. Future work will exploit this enhanced sensitivity to investigate cryptochrome photochemistry within a cellular environment. In complementary studies, HDX studies with mass spectrometric detection has allowed us to monitor blue-light induced conformational changes around the C-terminal tail (CTT) in the wild-type protein, which may be key to the signal transduction pathway in cryptochromes.

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Distance dependence of electron spin polarization and evolution in TEMPO free radical covalently linked to a pyrene moiety

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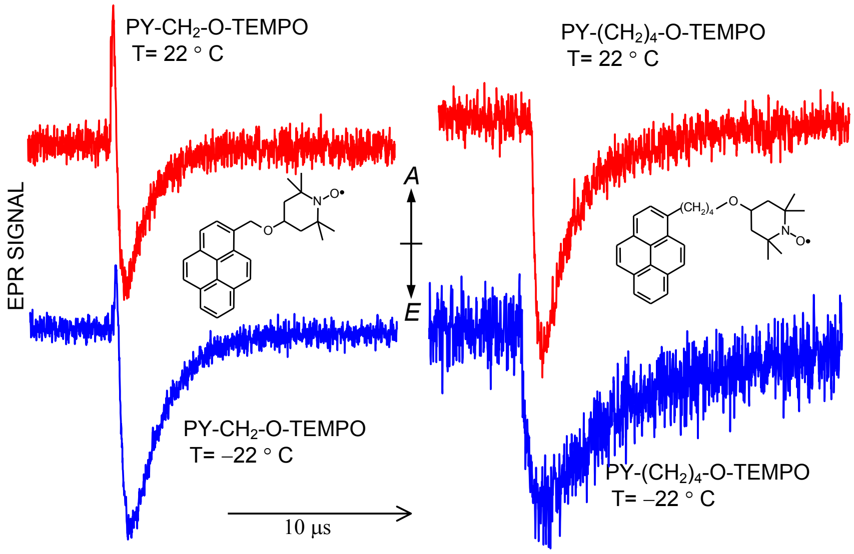
We report here our work on the distance dependence of the electron spin polarization of 2,2,6,6-tetramethyl piperidine *N*-oxyl (TEMPO) free radical covalently linked to a pyrene moiety through a spacer group of different lengths, in solution. Because of the covalent linkage, diffusive motions between the two moieties are severely restricted. In our earlier work, we showed that in naphthalene–spacer–TEMPO systems, the singlet state and the triplet state of naphthalene undergo sequential quenching by the TEMPO moiety, producing, respectively, enhanced absorptive (A) and emissive (E) electron spin polarization (ESP), the former diminishing with the distance [1,2]. The return of the polarized electron paramagnetic resonance (EPR) signal to the thermal signal is controlled primarily by the spin-lattice relaxation time of TEMPO. Unlike naphthalene, since pyrene has a very long singlet-state lifetime, the detailed spin dynamics and ESP in pyrene–spacer–TEMPO systems could be different from that of naphthalene–spacer–TEMPO systems.

So far we have synthesized PY–CH_2–O-TEMPO and PY–$(CH_2)_4$–O-TEMPO (for the structures, see Figure) and studied their spin dynamics, in *n*-hexane solution, after the photoexcitation of the pyrene moiety by a 266-nm laser pulse, at a temperature of 22 °C and low temperature of about −22 °C. Syntheses of such linked molecules with other spacer lengths are in progress. The time evolution of the EPR signals of the low-field hyperfine line of these two pyrene–TEMPO linked molecules is shown in the Figure. For PY–CH_2–O-TEMPO, a strong absorptive signal followed by an emissive signal was seen, corresponding to the sequential quenching of the singlet and the triplet states of pyrene. The ESP generation due to the singlet quenching decreased at low temperature. For PY–$(CH_2)_4$–O-TEMPO, ESP due to only the triplet quenching was seen at all temperatures. Unlike the naphthalene–TEMPO linked molecules, for both the pyrene–TEMPO molecules, the return of the spin-polarized EPR signal to the thermal signal was controlled largely by the lifetime of the pyrene moiety.



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Chemical amplification of magnetic field effects relevant to avian magnetoreception

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It is well known that many animals use the Earth's magnetic field to navigate [1]. The most likely explanation for their compass sense is based on the radical pair mechanism [2], which is thought to operate in cryptochrome flavoproteins in the retina [3]. Within this framework, magnetic field effects (MFEs) may alter the rate and yield of chemical reactions involving spin-correlated radical pairs as intermediates.

As pronounced directional responses of a radical pair reaction to an Earth-strength magnetic field (about $50\,\mu$T) at physiological temperatures are unexpected, it seems at first sight unlikely that such small effects could form the basis of a viable compass. However, evolution might well have availed itself of any opportunity to boost the sensitivity of the primary response so as to optimize the compass.

Here we show that under continuous photoexcitation, the primary magnetic field effect is indeed amplified chemically by slow radical termination reactions [4]. The nature and origin of the amplification are revealed by studies of model radical pairs such as FMN/tryptophan, FMN/ascorbic acid and indeed in the cryptochrome itself.

Additionally, significant amplification was observed at low field, which could potentially have an impact on the viability of a cryptochrome-based magnetic compass sensor.

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Crystal-structure dependence of quantum rotor induced polarization

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Methyl groups are abundant in organic and biological samples and thus are an object of investigation in the structure elucidation. Hence, obtaining hyperpolarization by such groups might be a valuable tool for structural and dynamical studies. For some molecules it is in fact possible to exploit the properties of the methyl group itself via so called quantum rotor induced polarization (QRIP). Here a non-Boltzmann distribution of nuclear spin states is generated due to their link to rotational quantum states and tunnelling phenomena at very low temperatures. The yielded signal enhancement was first observed in γ-picoline after a sudden temperature jump from 8 to 30 K [1]. When cooled down to liquid helium temperature (4.2 K) and then heated up by adding solvent at room temperature, an increase of the methyl carbon signal with an unusual signal pattern (proton coupled) can be observed in the liquid state [2]. The underlying mechanism was further explained as cross relaxation processes, which lead to observable magnetization [3]. However, this phenomenon is rare in other compounds and the investigation on homologues of γ-picoline suggests that similarity on a molecular level does not explain the occurrence or absence of the QRIP effect [4]. It is therefore proposed that the tunnel splitting, which plays a crucial role, is strongly dependent on the intermolecular interactions and the surrounding of the observed methyl group in the crystal structure [5]. Of particular interest are coupled methyl rotors. Hence, samples with small intermolecular methyl-methyl distances are currently investigated systematically and crystal structures of already measured samples are compared to identify contributing factors to QRIP.

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The solid-state photo-CIDNP effect of aureochrome LOV-C287S studied by ^{13}C MAS NMR

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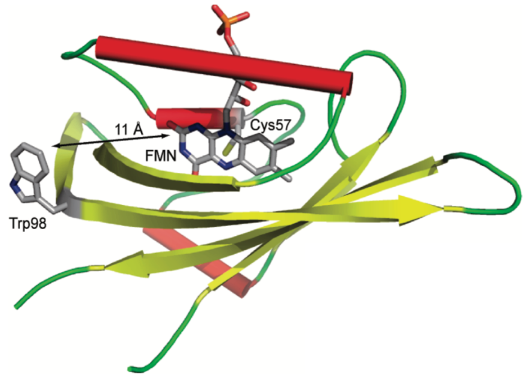
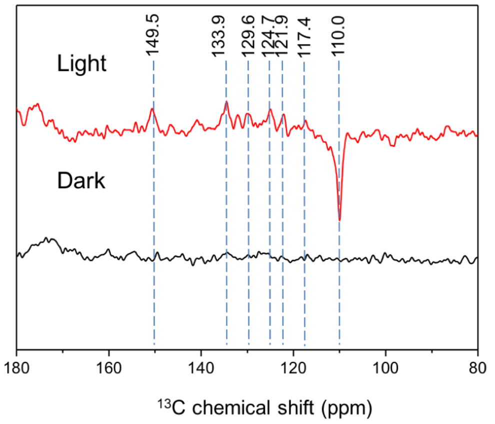
The solid-state photo-CIDNP effect is the occurrence of non-Boltzmann nuclear spin polarization upon illumination by radical-pair dynamics, which is detected by solid-state NMR as significantly enhanced absorptive or emissive signals. The solid-state photo-CIDNP effect [1], was found in 1994 by Zysmilich and McDermott [2] by continuous illumination of frozen and quinone-blocked natural photosynthetic reaction centers under magic-angle spinning (MAS) NMR conditions. Later, the solid-state photo-CIDNP effect has also been demonstrated in the flavin-containing protein phototropin LOV1-C57S [3].

Aureochrome is another class of biological blue-light receptors that contain flavin mononucleotide (FMN) as chromophore in its light-oxygen-voltage (LOV) domain. FMN absorbs UV-A/blue light and induce an intermediate flavin-cysteinyl adduct formation with a conserved cysteine in the natural-occurring LOV domain. A mutation in aureochrome-LOV (C287S) abolishes the adduct formation and generates a solid-state photo-CIDNP effect in MAS NMR. More flavoproteins are expected to show such effect when modified in a similar way.

Given that the adduct formation is abolished, the lifetime of ^{3}FMN is thus increased, which further induces a less competitive electron transfer from a distant (11 Å edge-to-edge) tryptophan (Trp) to FMN. A tentative photo-cycle involving the generation of a spin-correlated radical pair [$FMN^{-\bullet}-Trp^{+\bullet}$] is proposed. The origin of solid-state photo-CIDNP effect in flavoprotein system is presently investigated by employing aureochrome LOV-C287S as a model.





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TR CIDNP study of sensitized photo-oxidation of thymine and thymidine in aqueous solution

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At present, there is great interest in model studies of the processes of one-electron oxidation of DNA bases, since there are evidences that such processes occur in a living cell. The one-electron oxidation of DNA duplex results in the formation of a nucleobase cation radical that is subsequently consumed in chemical reactions that often lead to mutations. The electron transfer processes occur mainly involving guanine – the nucleic base with the lowest oxidation potential. However, there is evidence that in some cases in oligonucleotides that lack guanines, reactions occur also with the participation of other DNA bases, as well as thymine. While direct absorption of UV light leads mainly to the formation of pyrimidine dimers, an interaction of UV light with DNA bases in the presence of photosensitizers leads to the formation of short-lived nucleotide radicals, including thymine radicals. Further work is however required in order to establish the detailed mechanisms of photosensitized formation of the short-lived radical intermediate and its characterization at physiological conditions. We found only limited examples of the detection of radicals derived from thymine and thymidine in solution by means of conventionally used EPR and transient absoption techniques.

In the present work, we used the TR CIDNP technique for studying the photoinduced oxidation of thymine, T, and its nucleoside thymidine, dT, in the expectation that the information obtained will provide a basis for understanding reactions associated with electron removal from this class of compounds in DNA. We chose two common-used photosensitizers for the radical generation: 2,2’-dipyridyl (DP) and a water-soluble derivative of benzophenone, namely 3,3’,4,4’-tetracarboxy benzophenone (TCBP). The pH-dependences of geminate CIDNP was explained in terms of reactants pK_a values. A complimentary analysis of the pH-dependences of geminate CIDNP and CIDNP kinetics obtained for the reactions of T and dT with triplet-excited TCBP (DP) at wide pH range enabled us to get information on transient radical intermediates of T and dT, and to establish detailed mechanisms for the reactions studied. For the reaction of thymine or thymidine with triplet-excited DP the formation of (5m-H) radical was shown. In acidic and neutral solutions the reaction of thymine or thymidine (at acidic pH) with triplet-excited TCBP proceeds via electron transfer followed by fast deprotonation of thymine (thymidine) cation-radical or by proton-coupled electron transfer with the formation of neutral (N3-H) thymine (thymidine) radical. In strongly basic solution the formation of thymine anion radical is shown.

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Photo-chemical and spin-chemical studies on inclusion systems: a series of sulfonated anthraquinones and cyclodextrins

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The photo-physics and photo-chemistry of crown ethers have been extensively studied over several years. Cyclodextrin (CD), as one of them, can be used as model enzyme and its unique reactional cavity provides specific photochemical properties. The β-, and γ-CDs' specific inclusion properties and dynamic behaviors [1,2] have been studied so far, nevertheless, the α-CD is not well known yet. In this work, the photochemical reaction in α-CD comparing with β-, and γ-CD is investigated using a time-resolved EPR method. The chemically induced dynamic electron polarization (CIDEP) spectra show four groups of CD radicals with specific hyperfine coupling (hfc) constants, due to the main reaction pathway of the hydrogen abstraction from the CD molecule and the ejection of the transient radical of AQSs [3]. These are tentatively assigned to free radicals of AQSs and CDs formed inside of the CD cavity, where triplet mechanism (TM) and radical pair mechanism (RPM) were observed. By analyzing the spectral pattern and time domain, the photochemical properties and dynamic information of the inclusion system formed by AQSs and CDs are identified. It is considered that in the smallest size α-CD condition, separation of transient radicals is weak or diffusional motion is slow so that RPM exhibits dominant, in where CIDEP spectra contributed by the hyperfine-dependent spin polarization of (S-T_-) RPM might be observed. However, in the larger CD conditions, free radical spectral pattern express mainly. The details of dynamic information and spectral analysis will be presented.

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Anisotropic magnetic field effects in the solid state by fluorescence

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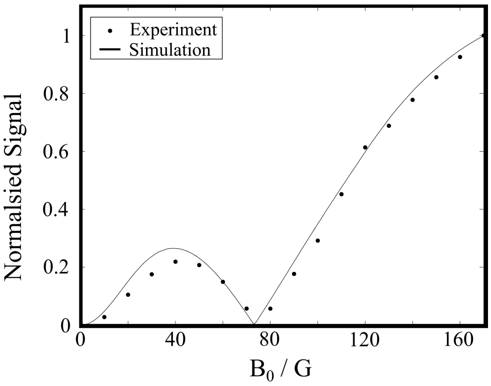
Merrifield *et al.* researched the effects of magnetic fields (both in terms of strength and direction) on the delayed fluorescence intensity of photo-excited single anthracene and tetracene crystals [1,2]. Whilst these previous studies were restricted to fields exceeding 400 G, we expand our investigations to much weaker magnetic fields.

The angle-modulated experiment for lock-in amplification (AMELIA) is a custom-built spectrometer, purpose-designed for the detection of anisotropic magnetic field effects (MFEs) in fluorescing photo-excited samples. A solid sample, typically a single crystal, is placed into a slowly rotating magnetic field and the modulation of the fluorescence is recorded under conditions of continuous illumination and by lock-in amplification. The resulting signal is a voltage proportional to the modulation depth of the fluorescence intensity. The alteration of the applied field orientation is slow on the timescale of the triplet exciton dynamics such that the signal is proportional to the steady-state fluorescence for a given field direction. Here we present our data obtained on single crystalline anthracene and tetracene – chosen because they provide an ordered array of molecules that are well understood. Simulations verify the results obtained from experiment.

Future work will be aimed at expanding the scope of experimentation to less ordered media, such as films and photoselectively-excited frozen solutions, as well as modifying the setup to allow for measurements at very low field strengths.



A comparison of the experimental and simulation results for the ac’ plane of tetracene.

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Field-cycling photo-CIDNP MAS NMR on a photosynthetic reaction center

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Nuclear spin hyperpolarization readily occurs during the light-induced photosynthetic charge separation processes in nature. It manifests itself, amongst others, in solid-state photo-chemical induced nuclear polarization (photo-CIDNP) in photosynthetic reaction centers [1]. So far, this phenomenon has been observed at a magnetic field range between 1.4 T and 17.6 T which allowed probing the field dependence of the solid-state photo-CIDNP effect via ^{13}C MAS NMR [2,3]. The study of the effect at different magnetic fields allows for determination of the mechanism producing the spin-hyperpolarization as well as of the electronic structure of the cofactors inside the proteins responsible for the charge separation process [2]. Since the effect has been predicted to have functional relevance in regulating electron transport, its study of even lower magnetic fields down to Earth magnetic field is of further interest [4–6]. Since lower magnetic fields are accompanied by lower spectral resolution, field-cycling techniques need to be employed allowing to induce the effect at low fields, while recording the MAS NMR spectra at high magnetic fields.

Here we present a study of the solid-state ^{13}C photo-CIDNP effect on selectively isotope labelled reaction centers of *Rhodobacter* (*R.*) *sphaeroides* WT between 0.25 T and 2.0 T by using an aerodynamic shuttle technique, which allows inducing the effect in the stray field of the magnet and measuring it at 9.4 T under MAS conditions. The study revealed a surprising sign change of the effect not predicted by theory so far.

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Magnetically sensitive light-induced reactions in Drosophila melanogaster proteins

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The spectroscopic characterization of the radicals and radical pairs in fruit fly cryptochrome in their different protonated and non-protonated flavin radical states has recently been described [1]. *Drosophila melanogaster* cryptochrome (*Dm*Cry) is one of the model proteins for animal blue-light photoreceptors. The cryptochrome/photolyase protein family contains a conserved triad of tryptophan molecules that transport electrons from the protein surface to the FAD cofactor. Recently an in-depth time-resolved optical and electron paramagnetic resonance spectroscopy study has revealed that an additional fourth, more distant, aromatic amino acid acts as the terminal electron donor [2,3]. The exchange of the fourth tryptophan for a phenylalanine molecule dramatically changes the lifetime of the excited species [2,3].

Magnetic field effects on the absorption of the excited-state radicals of *Dm*Cry (WT) (wild type) have recently been reported [4]. We describe how the magnetic field effect can be profiled by both nanosecond transient absorption at low temperatures and using highly sensitive broad-band cavity-enhanced absorption spectroscopy (BBCEAS) methods at higher temperatures.

*Dm*Cry derivatives, *Dm*Cry W394F (where a substitution is at the fourth tryptophan position) and *Dm*Cry W342F (where substitution is at the terminal tryptophan of the conserved triad) have been synthesized and characterized by the Freiburg group, to characterize the deactivation pathway in *Drosophila melanogaster* cryptochrome [1–3]. We show from our preliminary magnetic field effect experiments, that the *Dm*Cry W394F has a significantly enhanced magnetic field effect compared to the *Dm*Cry (WT) protein, with the magnetic field effect dramatically increasing from 5% to 30% at 230 K. In addition the *Dm*Cry W342F shows no magnetic field effect, and has no long-lived radical state, in agreement with published results [1]. With more sensitive absorption and fluorescence methods being developed within the research groups, we plan to profile the magnetic response of these proteins at lower and lower field strengths, to determine the optimal chemical structures and optical properties required to develop a room temperature molecular magnetosensor at the Earth's magnetic field strength.

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Disrupting the avian compass. Radiofrequency magnetic field effects on radical pair reactions

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In 2004, it was observed that the magnetic compass orientation behavior of migratory birds could be disrupted by weak time-dependent magnetic fields [1]. A number of further experimental tests have corroborated this observation, and the perturbation of the birds' magnetic sense by oscillatory magnetic fields is often invoked as a direct piece of evidence for the radical-pair hypothesis of magnetoreception. This hypothesis cites a magnetic field-dependent chemical reaction involving a pair of spin-correlated radicals as being the primary sensing mechanism providing the directional information used in compass orientation. The observed effect of time-dependent magnetic fields is usually interpreted as a direct resonance effect on the spin dynamics of the sensing radical pair reaction. However, this explanation is not without controversy, with some contradictory experimental results and scepticism surrounding requirements for extraordinarily long spin coherence lifetimes.

Modelling radical pairs subject to these experimental conditions represents a significant challenge. We present a brief outline of a novel computational approach involving a reformulation of Floquet theory that allows us to treat large, complex radical pairs in the presence of a time-dependent magnetic field [2]. With the ability to model the desired conditions, we explore the results of the various orientation experiments in the framework of the radical pair hypothesis to discuss the implications of the findings on our understanding of the underlying mechanism.

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A single molecule based approach to radical pair mechanism

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Migratory birds are able to reach their long-distance goal by sensing the geomagnetic field. The mechanism of how these birds can sense such remarkably weak magnetic fields and resolve their orientation is an unsolved problem. The key candidate molecule believed to be responsible for this ability is a photoreceptor protein called cryptochrome [1]. Cryptochrome is present in the cone membrane disc in the retina of the bird's eye and binds to the flavin adenine dinucleotide (FAD) molecule dye. The FAD can absorb UV or blue light and form a radical pair (RP), which can interact with the magnetic field. As a result, changes in the signaling state of the protein are believed to occur. This hypothesis has not yet been proven, however, despite the large number of studies being conducted over a long period of time [2]. An area that has hitherto remained uninvestigated, is direct measurement of cryptochrome photochemistry at the cellular level.

Therefore, in this study, we decided to develop a single molecule based microscope to investigate whether photochemical processes in living cells are affected by an applied magnetic field. Since the single molecule technique measures individual molecules, it is possible to investigate the field effect on molecules that can not be obtained by measurements on ensemble averages. Individual RPs differ in their initial hyperfine states and can show different magnetic field sensitivity. It is conceivable that the bird can spatially distinguish between different cryptochrome molecules across the retina and therefore selectively extract information from the most magnetically sensitive pairs. Although there are many different techniques for detecting single molecules, we make use of a total internal reflection fluorescence (TIRF) microscope arrangement due to its simplicity and convenience [3] and the fact that it provides open access to the sample to allow us to introduce magnetic fields of different magnitudes, frequencies and orientations. Here we present our development of the instrumentation designed to measure the effect of applied magnetic fields on individual flavin-based RPs.

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P21

Broadband cavity-enhanced absorption spectroscopy measurements of magnetic field effects

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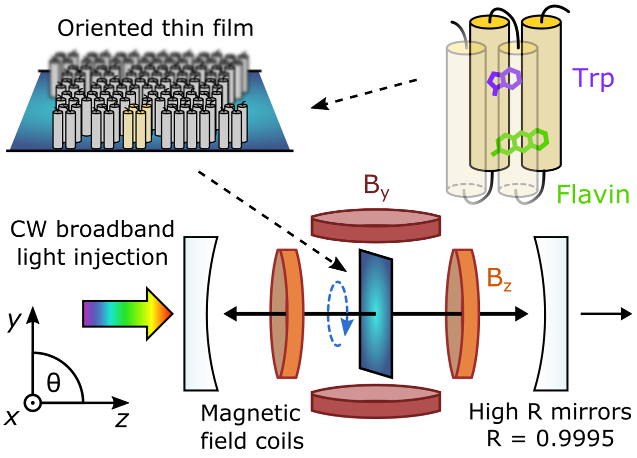
There exists a variety of magnetosensitive chemical systems, the investigation of which is of great interest to the fields of avian magnetoreception, electron spin resonance and semiconductor research. These systems usually are comprised of a photoinduced pair of radical species, which undergoes a coherent spin-state evolution (singlet ↔ triplet), the rate of which is altered by the presence of the magnetic fields. The magnetically altered yield of such a chemical reaction (photocycle) and its kinetics can be probed optically by measuring the transient change in spectral absorbance of the sample following flash photoexcitation as a function of applied magnetic field.

Here, we present a time-resolved variant of broadband cavity enhanced absorption spectroscopy (BBCEAS) [1], which uses a pulsed photoexcitation source (Nd:YAG pumped dye laser) and an array or photomultiplier tubes in order to achieve a nanosecond time resolution of the measurement. We also introduce the maquette – a biomimetic protein model system for the cryptochrome molecule [2], which is suspected to be the core of animal magnetoreception mechanism. This *de novo* protein is an electrostatic ensemble of four α-helices, which can be easily functionalized and modified to investigate different electron transfer conditions. Furthermore, maquette molecules can be easily oriented on the surface of a thin film. This dimensionality reduction (from 3D liquid to 2D oriented film) is proposed as a mean to investigate the anisotropy of the magnetic field effects on the maquette system, to obtain an insight into the mechanism of anisotropic field effects in the cryptochrome molecule.



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Teaching spin chemistry to dummies. The significance of rubber ducks in contemporary spin chemistry

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The significance of rubber ducks in contemporary American culture has been subject to academic discourse [1]. Similarly well-known is their importance for oceanography, although originally rather accidentially [2]. However, their equally important significance in contemporary spin chemistry and in particular to the future of the spin chemistry community has been largely neglegted.

As apparent already from the title of this meeting, "International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena", spin chemistry, despite its name, is not restricted to chemistry and physics. The seminal review by Steiner and Ulrich [3] is still the starting point for many students of the field nowadays. Nevertheless, the concepts described there are sometimes rediscovered independently decades later in different areas of research. This can be explained easily by missing knowledge of fundamental concepts of spin chemistry outside the rather small community. Nevertheless, it could well have some impact on the perception of the field that was thought to be left behind [4].

Karl Kuckuck and Bärbel Bollenhut, the two famous Black-Forest rubber ducks, dressed-up for SCM 2017.

Therefore, we propose a completely different approach to teach spin chemistry [5], complementary to the seminal review [3]. This is of particular importance given the interdisciplinary relevance of spin chemistry due to its proposed role in the magnetic compass sense of living organisms [6]. We are confident that our approach helps the spin chemistry community to broaden its impact on the scientific community as a whole, and to get those unfamiliar with fundamental concepts started quickly and quackly.

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Radical polarization and liquid-state dynamic nuclear polarization (DNP) with photo-excited fullerene nitroxide derivatives

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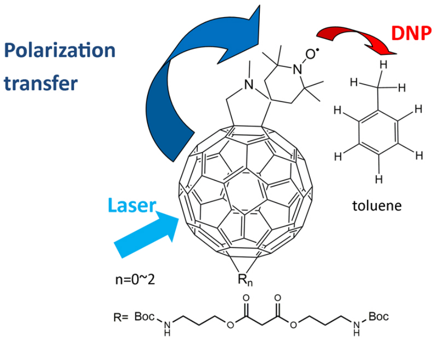
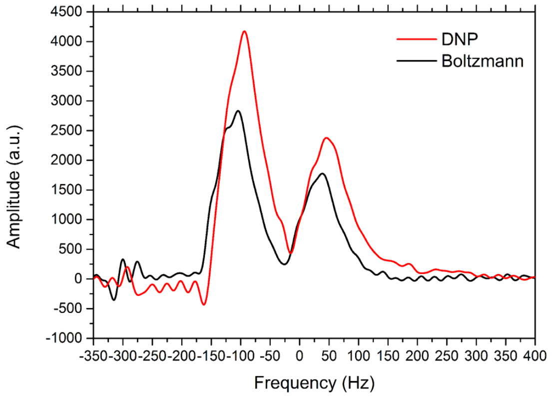
Nuclear magnetic resonance (NMR) is a fundamental spectroscopy to study biological systems and materials. It detects the interaction between magnetic nuclei and their surrounding at very low energy scale, therefore it is a non-invasive tool to study a variety of objects *in vitro* and *in vivo*. However, the low sensitivity of NMR, due to these small energies involved, has been a significant obstacle [1]. Dynamic nuclear polarization (DNP) has been established as a method to enhance NMR signals in solution and solid state, by transferring the polarization from unpaired electron to nuclear spins. Herein, we report on radical polarization and Overhauser type DNP performance of nitroxide radicals functionalized by photoexcitable fullerene derivatives in liquids. Fullerene-nitroxide (FN) consists of a pyrrolidine linkage between a C_{60} and a nitroxide, proposed by Covaja *et al.* [2]. Additional malonate derivatives increase the electron spin-lattice relaxation (T_{1e}) and solubility in water. Large electron spin saturation factors of FN derivatives radical are observed by conventional DNP with microwave, at either 0.34 T/9.8 GHz or 1.2 T/34 GHz [3]. In addition, pulse laser excitation of the FN derivatives leads to a transient nitroxide radical polarization, which is at least one order of magnitude larger than Boltzmann equilibrium. Overhauser ^{1}H-NMR signal enhancements of the toluene solvent were observed under steady-state illumination of FN derivatives [4]. With these observations, the ^{1}H-NMR signal of toluene in liquids can be enhanced by optical polarizing FN derivatives. Optimization of optical-polarized DNP will be discussed and could offer an easy-to-implement approach to enhance NMR signal than other conventional methods.





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Radical pair dynamics on a protein surface probed by pulsed magnetic field effects

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In the system of 2,6-AQDS and hen egg white lysozyme (HEWL), a large magnetic field effect (MFE) was observed and is rationalized by a Coulomb attractive interaction between the negatively charged AQDS radical and the positively charged protein surface [1]. By this it was demonstrated that the photochemical reaction and its MFE can be used as a probe of the protein surface interactions. The radical pair (RP) produced by laser flash photolysis is initially in a triplet state. The part of triplet RP becomes singlet RP by spin mixing and returns to the ground state by charge recombination or diffuses to be a free radical (FR). Since the magnetic field reduces the efficiency of spin mixing, transient absorption of RP and FR increases. By the RP mechanism, the MFE is very sensitive to the dynamic feature of the radical diffusion on the surface of the protein. Therefore, the time domain measurement of the RP dynamics, *i.e.*, lifetime of RP is one of the most crucial factors for the discussion. However, the usual transient absorption measurements hardly distinguish the RP from the large background signal of the FR and the triplet excited state. The "switched external magnetic field" (SEMF) method enables us to measure the decay kinetics of the RP avoiding the interference by the background transient absorptions [2]. Here, we present the results by SEMF for HEWL / 2,6-AQDS systems.

Two types of the field switching pulse sequence, field ON-OFF (presence of the field $\Delta B = 21\,\mathrm{mT}$ to absence of the field) and OFF-ON (absence to presence) were operated for the kinetics of the RP at 21 mT and zero field, respectively, as shown in Figure 1. The delay time shift experiments (OFF-ON) clearly show that there are two components of the radical pair, one having a short lifetime ($\tau = 0.08\,\mu\mathrm{s}$) and the other having a long lifetime ($\tau = 0.43\,\mu\mathrm{s}$). Precise analysis of the salt concentration dependence of MFE and SEMF experiments and the UV-vis spectral data of the ground state results in the conclusion that the two radical pairs are produced in the different binding positions on the surface of HEWL and have individually different dynamics.

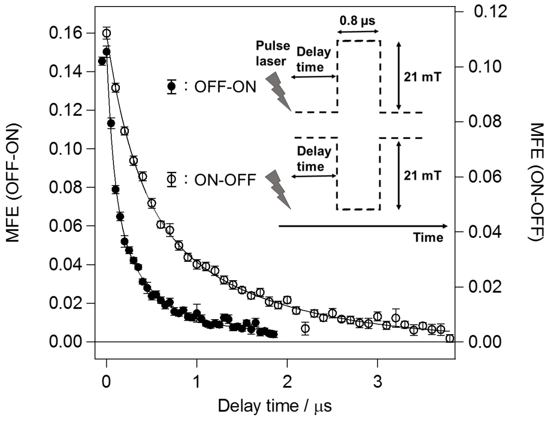

Figure 1: Measurement results of SEMF by the pulse sequences: OFF-ON and ON-OFF experiment.

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Laser flash photolysis study and magnetic field effect on different photoinduced reactions involving a therapeutically important small molecule with organic amines and semiconductors

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Photochemistry is concerned with the reactions involving electronically excited molecules. The fundamental process lying behind this excited-sate reaction is charge transfer (CT). Much attention has been devoted to the mimicry and understanding of CT processes like photoinduced electron transfer (PET) and excited-state proton transfer (ESPT) because they occur in a wide variety of biological systems. Magnetic field effect (MFE), a tool for identification of spin state and proximity of radical/radical ions, which are formed as reaction intermediates, have been found to play a pivotal role in resolution of these two photoinduced phenomena in presence of each other [1,2]. 9-aminoacridine hydrochloride hydrate (9AA-HCl), a prospective PDT drug, forms excimer in different confined medium with varying cavity size [3] and exists in neutral, singly protonated and doubly protonated forms [1]. Photoinduced interactions of 9AA-HCl with *N,N'*-dimethylaniline (DMA) reveal that ESPT and PET are the phenomenon that have been found to be involved whereas with triethylamine (TEA) ground-state complex formation, ground-state proton transfer and PET are prevalent. Further, electron accepting capacity of dimethyl viologen (1,1-dimethyl-4,4-bipyridinium, MV^{2+}) is utilized and make an attempt to prove that 9AA-HCl can act as electron donor in PET reactions. Moreover, participation of MV^{2+} in ESPT reactions while interacting with 9AA-HCl is also highlighted. It is observed that PET occurs in both homogeneous and heterogeneous media while ESPT occurs only in homogeneous medium and is prevented in micellar medium. Moreover, a hopping mechanism of electron transfer is established from the discrepancies of calculated and experimentally observed values of $B_{1/2}$. The integration of the two studies proves the dual role of 9AA-HCl in PET reactions in the presence of suitable electron donor or acceptor and under suitable condition of redox potentials. Moving forward, the fundamental understanding of PET between semiconductor nanocrystals and dye molecules is very important to design efficient light harvesting system based on inorganic-organic hybrid system. Therefore, considerable attention has been paid on ZnO based devices for potential applications in photonics such as nanolasers, solar cells, sensors, photodetectors among others due to their high photosensitivity, large bandgap and low cost [4]. The, participation of MV^{2+} in PET reactions during the interactions with ZnO NPs is being investigated by using laser flash photolysis study in the course of formation of $MV^{+\bullet}$. The occurrence of charge transfer along with the formation of transient ions indicates that the stability of CT complexes is much more prominent for 6.3-nm ZnO NPs with MV^{2+} than 4.2-nm ZnO NPs with MV^{2+}, which is due to its charge recombination rather than charge separation.

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Theoretical insights into the effects of radio-frequency fields on spin chemical systems

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Recent experiments have reported an effect of weak radiofrequency radiation in the MHz-range on the concentrations of reactive oxygen species (ROS) in living cells [1]. Since the energy that could possibly be deposited by the radiation is orders of magnitude smaller than the energy of molecular thermal motion, it was suggested that the effect was caused by the interaction of the radiation with transient radical pairs within the cells, affecting the ROS formation rates through the radical-pair mechanism. This poses the problem of how to predict the effect that radiation of a certain frequency and intensity would have on nanoscale biomolecular systems through underlying spin dynamics.

Here we suggest a possible recipe for a solution by developing a method for calculation of the quantum yield change as a function of radiation frequency and field strength, assuming the reaction pathways and rate constants of the specific spin system are known. The calculations root upon the rotating reference frame, which restricts the applicability of the method by the symmetry constraints [2]. In order to alleviate these constraints, an alternative method was also developed based on the time-dependent perturbation theory and the eigenspectrum of the unperturbed spin Hamiltonian [3]. The two independent methods for prediction of the effects of radiofrequency radiation on spin systems have been used to study simple radical pair systems to illuminate potential strengths and weaknesses of the theoretical formalisms in the case of more complicated biological systems.

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Out-of-phase ESEEM. Determination of radical–radical distances in light-active proteins and their implication for biological magnetoreception

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Proteins of the photolyase/cryptochrome family share a conserved tryptophan pathway to transport electrons from the protein surface to the photo- and redox-active flavin adenine dinucleotide (FAD) cofactor in the core of the protein [1]. In photolyases the fully reduced FADH^- cofactor serves as donor of a catalytically-active electron for repair of light-induced DNA lesions, while in cryptochromes the metastable semiquinone FAD radical represents the signalling state for different biological responses to blue light. Recent spectroscopic results suggest that the electron-transfer pathway is more diverse in terms of the number and amino-acid composition than commonly anticipated. In detail, certain members of the animal cryptochrome family might use a fourth, more surface-exposed amino-acid residue as final electron donor for signaling-state generation [2]. The different environment of this alternative, more distant aromatic residue could reflect the difference between a pure electron-transfer pathway in photolyases, and a long-time stabilization of the radical pair for, *e.g.*, magnetoreception in avian compasses.

Direct characterization of the excited radical-pair state can be achieved by transient EPR spectroscopy, which grants access to the $\mathbf{g}$ and $\mathbf{A}$ tensors of the radical-pair partners, as well as the dipolar and exchange coupling constants D and J. While pulsed electron-electron double resonance spectroscopy lacks the capability to directly measure electron-electron interactions of short-lived radical species, measurements of the out-of-phase electron-spin echo envelope modulation (oopESEEM) of laser flash induced spin-correlated radical pairs gives direct access to the dipolar and exchange interactions between the radical-pair partners [3–5]. Therefore distance measurements, and thereby an identification of the radical partner molecule can be accomplished.

Here, we present results of transient EPR and oopESEEM measurements of different members of the photolyase and cryptochrome family at X-band and Q-band microwave frequencies, which prove that different amino acids at various distances function as final electron donor in animal-type cryptochromes [6].

Part of the work presented here has been performed in collaboration with Kenichi Hitomi (†) and Elizabeth D. Getzoff from the Scripps Research Institute (La Jolla, CA, USA), and Stephanie Franz and Lars-Oliver Essen from the Philipps-Universität Marburg (Marburg, Germany).

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Quantum cognition using nuclear spins in the brain? Spin dynamics and relaxation processes of a calcium phosphate cluster

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A recent theory of "quantum cognition", presented in [1], is based upon quantum processing using ^{31}P nuclei in a calcium phosphate cluster in the brain. An important requirement for this is that long-lived entangled nuclear singlet states exist in this molecule, $Ca_9(PO_4)_6$, known as Posner's cluster (see Figure 1). It has been suggested in [1] that its singlet nuclear spin coherence time may be of the order of 10^5 s ($\approx$1 day), which would be remarkably long-lived nuclear singlet coherence. The aim of the computational work presented here is to set an upper limit on nuclear singlet lifetimes in this cluster.

Conditions for singlet-based spin states to be long-lived with respect to J-couplings (which will be the principal source of coherent spin dynamics in the geomagnetic field) were identified, and it was found that a singlet state involving a trans pair of ^{31}P nuclei can be time-independent with respect to these couplings. The effect of dipolar coupling between the ^{31}P nuclei within the cluster on spin relaxation was investigated using Redfield theory, employing a similar method to that in [3]. The analytic relaxation superoperator was calculated in the extreme narrowing limit, and using this an expression for singlet relaxation rates due to modulation of intramolecular dipolar coupling by isotropic rotational diffusion was derived.

It was found that this will cause singlet relaxation on a timescale of 10^3 s (up to an hour), which is much less than suggested in [1]. Furthermore, intramolecular dipolar relaxation is only one of many possible relaxation routes, and so these results represent an upper limit on the singlet coherence time. Finally, taking an approach similar to that in [4], long-lived spin states (immune to dipolar relaxation) were identified by finding the eigenvalues of the relaxation superoperator. As well as intramolecular entanglement, some initial work has been completed on singlet lifetimes of entangled pairs of clusters.

The results presented in this poster identify states that are predicted to be long-lived in Posner's cluster, and suggest it is unlikely that singlet states within the cluster will persist over as long a timescale as suggested in [1].

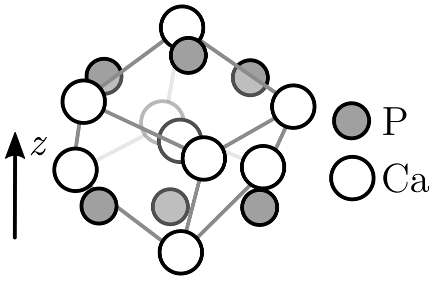

Figure 1: The structure of Posner's cluster, $Ca_9(PO_4)_6$, is thought to be based upon a near-body-centered cubic arrangement of calcium ions, with orthophosphate ions located on each of the faces of the cube. This arrangement means there is a rough octahedron of ^{31}P nuclei. The cartoon structure shown is based upon coordinates in [2], where the z-axis is a threefold rotation axis (only the calcium and phosphorus nuclei are shown).

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5-deaza-FMN as an alternative photo-sensitizer to FMN

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It has been shown that photo-CIDNP spectroscopy can serve as an excellent method to probe the electronic structure of elusive radicals in radical pairs [1]. A commonly used photo-sensitizer, bearing a significant biological importance, is flavin mononucleotide (FMN). FMN and its derivatives, such as riboflavin and flavin adenine dinucleotide (FAD), provide a versatile redox chemistry, while also being excellent chromophores. Due to these properties, flavins act as redox-active cofactors in a variety of enzymes, such as photoreceptor proteins like LOV domains or cryptochromes [2,3].

Apart from the main representatives of the flavin family, a plethora of analogues exists, structurally altered to fulfil a specific catalytic purpose. A particularly interesting group are the so-called deaza-flavins, in which one or more nitrogen atoms of the isoalloxazine moiety are replaced by an isoelectronic C–H group. These flavins are believed to lack the ability to perform one-electron redox reactions, due to instability of the resulting radical, at least in a "dark" protein environment [4].

In this work, the capabilities of 5-deaza-FMN as an alternative flavin photo-sensitizer are explored and compared to those of FMN. Photo-CIDNP spectroscopy, assisted by DFT calculations, grants insight into the electronic structures of the respective radicals observed in spin-correlated radical pair reactions with aromatic amino acids like tyrosine. Also, isotropic hyperfine coupling constants can be readily determined from time-resolved CIDNP experiments.

Understanding the photo-physical properties of 5-deaza-FMN offers a great opportunity to perform mechanistic studies of FMN-containing proteins, by replacing the cofactor with the structurally similiar, however chemically different, deaza-analogue.

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Optical detection of magnetic field dependent singlet–triplet interconversion in OLEDs

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In organic light emitting diodes (OLEDs), excited states are formed by non-geminate recombination following the injection of spin-up and spin-down charge carriers at metal-organic interfaces. Due to the equal contribution of injected up and down spins, excited singlet and triplet states are intrinsically formed without the need of any intersystem crossing process. Hence, OLEDs are an interesting toolbox to investigate spin-dependent radical and radical-pair processes.

While the excited singlet state can directly couple radiatively to the singlet ground state, triplet states are usually dark states. However, we are able to obtain an insight into spin statistics by using a novel class of emitter as dopant, which show simultaneous singlet (fluorescence) and triplet emission (phosphorescence) [1]. By applying an external magnetic field to the OLEDs, the spin dependent processes can be manipulated leading to a change in the spin statistics.

There are two distinct regimes: At low temperature and high magnetic field – according to the Boltzmann statistics – the spin-up and spin-down charges undergo a thermal relaxation ending up in a polarization with a bias toward spins aligned parallel to the external field. Here, we observe an increase in triplet and a decrease of singlet emission, which fits perfectly to theory [2]. Furthermore, we identify the Δg effect as an additional spin-mixing mechanism.

At a small magnetic field and especially at room temperature, thermal spin polarization cannot occur and the impact due to radical-pair reaction dominates. Recently, we have directly observed the hyperfine field induced singlet–triplet interconversion at small fields (<30 mT) by detecting the anti-correlation between fluorescence and phosphorescence (see Figure 1) [3].

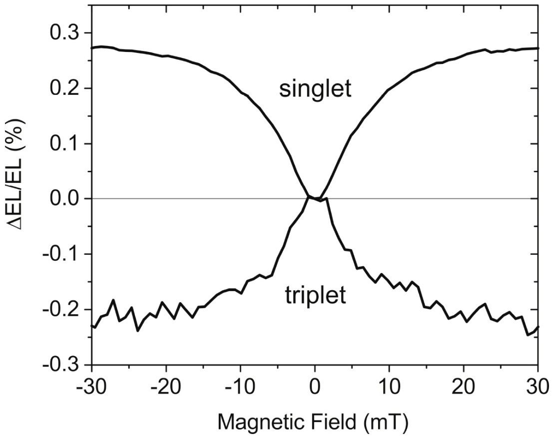

Figure 1: Magnetic field-dependent relative change of fluorescence and phosphorescence of an OLED doped with a dual singlet-triplet emitter. At zero field, the hyperfine interaction introduces a mixing between the spin states, which is suppressed when an external magnetic field is applied.

[1] W. Ratzke, L. Schmitt, H. Matsuoka, C. Bannwarth, M. Retegan, S. Bange, P. Klemm, F. Neese, S. Grimme, O. Schiemann, J.M. Lupton and S. Höger, *Journal of Physical Chemistry Letters* 7 (2016) 4802–4808.

[2] J. Wang, A. Chepelianskii, F. Gao and N.C. Greenham, *Nature Communications* 3 (2012) 1191.

[3] W. Ratzke, S. Bange, and J.M. Lupton, *manuscript under review*

SpecProFi: A toolbox for the processing and analysis of EPR data

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Fitting a model to the experimental data is almost always necessary to extract relevant physical parameters from EPR spectra. For complicated spectra comprising various magnetic interactions, such as hyperfine couplings or zero-field splittings, the parameter space can easily become very large. In these situations, the final fit result is often highly sensitive to the initial parameter guess, rendering the usual approach with gradients rather problematic. SpecProFi provides a series of strategies to overcome such problems, namely global fitting and uniform sampling of starting conditions. Simultaneously analyzing multiple datasets of the same sample obtained under different experimental conditions (*e.g.*, physical conditions of the sample, microwave frequencies) improves the least-squares surface of the parameter space and therefore the reliability of the obtained fit. To overcome the problem of local minima of the least-squares scoring function, a stochastic distribution of starting parameters with subsequent optimization has proven very powerful. For the distribution of starting parameters, SpecProFi uses either Monte-Carlo or Latin-Hypercube sampling, thus distributing the starting points homogeneously in an n-dimensional hypercube. Various optimization algorithms are available for the following least-squares minimization. To accelerate the time-demanding semi-stochastic analysis, parallel computing is implemented to distribute the optimization of different starting points. Additionally, an algorithm has been implemented that avoids the brute-force optimization of all starting points by making a pre-selection. All simulation routines used are based on the EasySpin program package [1].

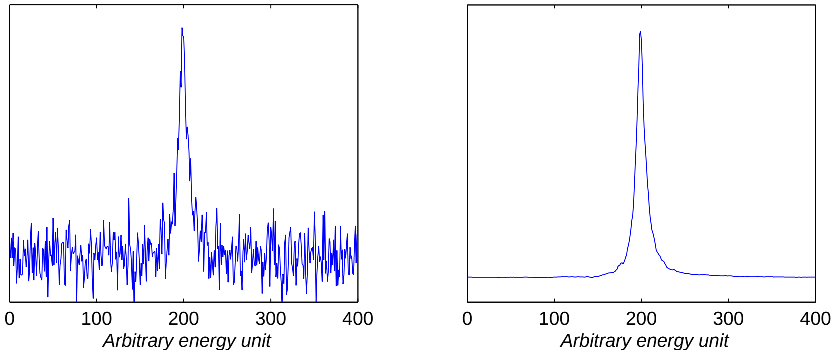

Figure 1: Denoising using a singular-value-decomposition-based method. (Left) Simulated signal, consisting of a single absorptive Lorentzian corrupted with Gaussian noise. (Right) Denoised signal using a SVD-based method.

Independent of the analysis procedures, various different useful data processing tools are available in SpecProFi. Denoising methods have been implemented using mathematical manipulations to improve the signal-to-noise ratio of experimental datasets (see Fig. 1). These methods are apodization and denoising based on either singular value decomposition (SVD) or wavelet transforms. Furthermore, automatic phase correction for cw-EPR data as well as differentiation methods like pseudo-modulation and derivatives stabilized with Tikhonov regularization are readily available.

[1] S. Stoll and A. Schweiger, *Journal of Magnetic Resonance* 178 (2006) 42–55.

Spin chemistry in donor–acceptor-substituted dipyrrinato-metal-complexes

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Magnetic field dependent transient absorption measurements of the charge-separated states (CSSs) of triarylamine-iridium(III)-dipyrrin-naphthalene diimide triads could show for the first time a biphasic magnetic field effect, which can be assigned to the transition from coherent to incoherent spin-motion at about 10 mT [1]. This interpretation was later again confirmed by reproduction of the decay-curves via solution of a fully quantum chemical model based on the stochastic Liouville equation [2].

In this study we focus on the influence of the central, metal-containing chromophore on the formation and the spin chemistry of CSSs. Therefore we synthesized two additional sets of dipyrrinato-metal complexes with varying central metal ions and complex geometry (see Figure 1). The complexes were characterized by magnetic field dependent transient absorption spectroscopy in the nanosecond time-regime at fields between 0 and 1800 mT and fitted to the proposed reaction scheme to obtain the magnetic field dependent value $k_{\pm}$.

The analysis of the experimental data shows that the central complex does indeed influence the photophysics and the spin-chemistry of the triads. For example, the lifetime of the charge-separated state is extended from 580 ns for Ir(III) to 1700 ns for Pt(II) and 1800 ns for Pd(II), while the magnetic field effect rises from a 6-times-increase in lifetime for Ir to a 35-times-increase for Pt and a 90-times-increase for Pd while the characteristic magnetic field strengths remain relatively unchanged. This corresponds to the stronger decrease in $k_{\pm}$ at higher fields and the relatively constant locations of the areas with lower slope which can be seen in Figure 1.

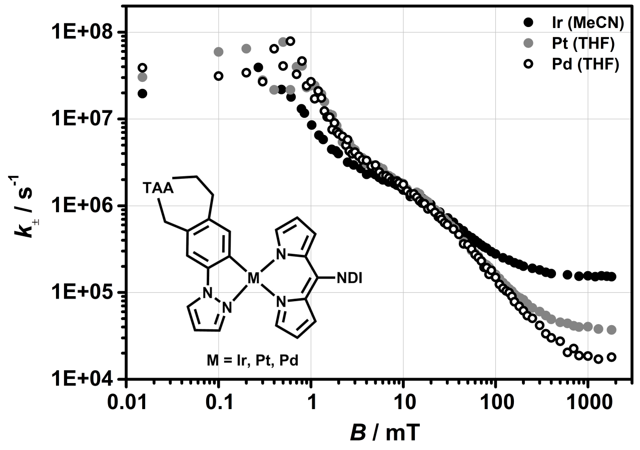

Figure 1: The magnetic field effect of the compounds investigated in this study.

[1] J.H. Klein, D. Schmidt, U.E. Steiner and C. Lambert, *Journal of the American Chemical Society* 137 (2015) 11011–11021.

[2] N.N. Lukzen, J.H. Klein, C. Lambert and U.E. Steiner, *Zeitschrift für Physikalische Chemie* 231 (2017) 197–223.

Chemically engineered native and polymeric carbon dots. In quest of origin of photoluminescence and aptitude for electron transfer corroborated by magnetic field effect

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Carbon dots (CDs) are known to have a wide range of applications, yet our understanding of their structure and chemistry remains ambiguous because of their highly complex nanostructured framework. Their nanoscale organization in conjunction with chemical functionalities possesses useful excitation dependent photoluminescence (EDPL) property, which violates Kasha-Vavilov rule of excitation-independent photoluminescence (EIDPL). However, we have attempted to establish the intrinsic mechanisms of EIDPL of CDs along with their molecular structure by newly synthesized Ru(III) and amine (ethylenediamine) doped CDs and highlighting free electron distribution on their surface, which facilitates photoinduced electron transfer (PET) [1] to a model quinone drug, menadione (MQ) producing $CD^{+\bullet}$ radical ions studied by laser flash photolysis corroborated with magnetic field of the order of $0.08\,\mathrm{T}$ [2]. We have also carried out similar experiments with polymeric carbon dots (pCDs) synthesized by cross linking the CDs with dithiothreitol (DTT). It has been found that intra-chain energy and electron transfer phenomena with pCDs are drastically different compared to the native dots. The PET from CDs and pCDs to MQ is further supported by enhancement of population of intermediate transient radical ions in presence of an external magnetic field of $0.08\,\mathrm{T}$ where both exchange interaction between geminate spin correlated free electrons and their hopping through π-electron cloud become operative. The anomaly between experimental and calculated $B_{1/2}$ values, the measure of hyperfine interactions present in the system, indicates the presence of highly conjugated π-electron cloud along with quite a good number of odd nuclei in native dots as well as pCDs and that is also the prime reason for producing EIDPL. By exploiting the PET process, we have also developed an important sensing platform for quantifying toxic and carcinogenic quinone derivatives in live HeLa cells that can be used for drug screening. To gain a more explicit picture of entire experimental findings, the formation mechanism, dynamics and photophysical properties of CDs and pCDs have been further investigated using molecular dynamics (MD) and DFT calculations where it is clearly demonstrated that CDs can act both as electron donor and acceptor along with their most probable electronic transitions from their surface to surface-tethered ligand.

[1] A. Sau, K. Bera, P. Mondal, B. Satpati and S. Basu, *Journal of Physical Chemistry C* 120 (2016) 26630–26636.

[2] K. Bera, A. Sau, P. Mondal, R. Mukherjee, D. Mookherjee, A. Metya, A. K. Kundu, D. Mandal, B. Satpati, O. Chakrabarti and S. Basu, *Chemistry of Materials* 28 (2016) 7404–7413.

The origin of magnetoconductance in solar cell of organic thin film using P3HT and PCBM

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Organic solar cells have many advantages such as light weight, flexibility of form, low cost for fabrication and so on. Therefore organic solar cells attract attention as next-generation devices and alternative to conventional silicon-type solar cells. Dissociation of excitons and generation and recombination of charged carriers occur in the junction area between the donor and the acceptor in the active layer of the cell. These reactions are important dynamics to determine the device performance. Magneto-conductance (MC), which is defined by a change of current density (J) induced by external magnetic field (B): $\mathrm{MC}\,(\%) = [J(B) - J(0)]/J(0) \times 100$, arises from the interplay between the spin-selective recombination and the B-field dependent spin conversion of spin pairs, so that the MC effect provides information about the carrier dynamics in organic solar cells under operating condition without destroying the device. Recently, the MC effect due to the hyperfine mechanism of geminate electron-hole (e-h) pairs in a single junction (SJ) solar cell consisting of pentacene and C_{60} clarifies the carrier recombination yield of 1% [1]. In bulk junction (BJ) solar cells using P3HT and PCBM, a similar positive narrow MC effect is observed in light. In addition, broad MC effects due to the Δg mechanism of e-h pairs, which are respectively negative below 1 T and positive above that, were also detected [2]. From the abstruse magnetic field dependence of MC effect it is suggested that that inhomogeneous junction structure affects the MC effect. Hence in this contribution we measured the MC effects for SJ- and BJ-cells with P3HT and PCBM in order to elucidate the mechanism of the MC effect.

Figure 1 represents the magnetic field dependence of MC effects measured in the absence of bias voltage in light. The BJ cell indicates two types of MC effects with narrow and broad half-fields ($B_{1/2}$) that are respectively called by MC_1 and MC_3, while the SJ cell shows no clear effect. Since the observed lineshape of light MC effects for the BJ cell is basically the same as reported [2], the MC1 and MC3 may be respectively caused by the hyperfine and Δg mechanisms of e-h pair. In the dark state of the SJ cell, on the other hand, three MC effects with different $B_{1/2}$ values of 2–6, 20–40 and more than 400 mT which are named as MC_1, MC_2 and MC_3 in order, were observed.

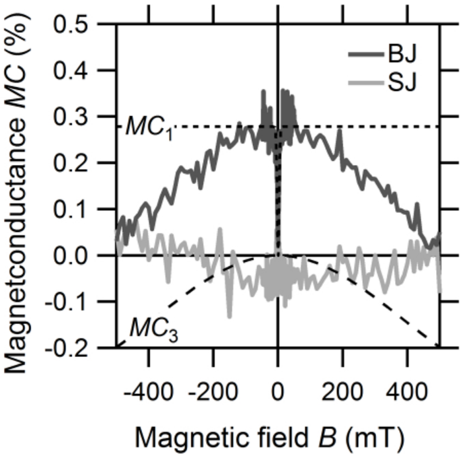

Figure 1: Magnetic field dependences for the MC effect observed in light. The broken curves are two components fitting the MC of BJ cell.

[1] T. Omori, Y. Wakikawa, T. Miura, Y. Yamaguchi, K. Nakayama and T. Ikoma, *Journal of Physical Chemistry C* 118 (2014) 28418–28424.

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Spin-dependent chemistry at III-V semiconductors

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The conduction band electrons of a p-type III-V semiconductor, such as gallium arsenide (GaAs) can be polarized with circularly polarized light. The orientation of this polarization, "up" or "down", can be influenced by switching between right- and left-circular light [1]. In electrochemical systems, it is possible to transfer these photoelectrons from the conduction band across the electrochemical interface to a redox mediator in solution. If the solution species is paramagnetic, such as methyl viologen radical ($MV^{+\bullet}$), applying an external magnetic field (B_0) orients the electrons spins preferentially along B_0. We can expect from the Pauli exclusion principle that spin orientation affects the reduction current, as the transfer of an electron from the conduction band to the $MV^{+\bullet}$ is forbidden for spins of the same orientation and favored for the opposite orientation. It thus becomes possible to modulate the reduction current by modulating the helicity of the exciting laser light. Due to the relatively low polarization (P) of the electron spins within the GaAs conduction band ($P = 0.1$), and of the $MV^{+\bullet}$ radicals in solution ($P = 0.005$ at $1.5\,\mathrm{T}$), the current modulation is only quantifiable by lock-in detection [2].

One of the prerequisites for a successful experiment is that the current is limited by the number of electrons within the conduction band, implying that very low laser powers are required. In this poster the behavior p-GaAs is studied in terms of charge transfer kinetics and thermodynamics of the electrochemical interface under weak laser excitation and varying applied voltages in order to find the optimal conditions for spin-dependent electrochemistry. Also, possible methods are discussed to overcome challenges related to the p-GaAs electrochemistry, namely the instability of the electrode material and the presence of surface states.

[1] C. Weisbuch and C. Hermann, *Physical Review B* 15 (1977) 816–822.

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Investigation of spin states in organic light-emitting diodes based on thermally activated delayed fluorescence via multi-frequency magnetic resonance techniques

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and Vladimir Dyakonov[1,2]

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The mechanism of thermally activated delayed fluorescence (TADF) emission in organic light emitting diodes (OLEDs) raised many questions about the mechanism of triplet–singlet up-conversion leading to exciplex emission. Direct spin-sensitive measurements on OLED devices are scarce in literature. Here, we apply multi-frequency electroluminescence and electrically detected magnetic resonance (ELDMR, EDMR) to efficient TADF OLED devices based on exciplex emitters like 4,4',4''-tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (m-MTDATA) and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB). The idea behind these experiments is that the static magnetic field applied to devices under test modifies only the energy levels of triplet states due to Zeeman splitting, thus changing the emission rates. We observed that resonant microwave radiation, applied to OLEDs by a stripline, led to enhancement of the electroluminescence intensity. The effect was found to be very sensitive to experimental conditions, thus modifying the resonance frequency, temperature and microwave power we were able to shed some light on the underlying mechanism of the reverse intersystem crossing and the spin states involved. With temperature-dependent ELDMR, the singlet–triplet splitting ΔE_{ST} can be determined, as we reported in [1] for similar TADF systems. Comparing ELDMR, EDMR and photoluminescence detected magnetic resonance (PLDMR), we reveal differences in TADF processes under optical excitation and electrical injection. The information gained from magnetic resonance techniques can potentially help to design new cost-effective OLED materials as well as to further improve their performance.

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Para-to-ortho conversion of dissolved parahydrogen

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Parahydrogen (p-H_2) induced polarization (PHIP) [1,2] promises to be a simple and cost-efficient method to produce hyperpolarized agents for magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR). The signal enhancement is generated by exploiting the spin order of p-H_2-enriched H_2 gas. Here, we report *para*-to-*ortho* conversion (POC) times of p-H_2 in aqueous solutions with and without a hydrogenation catalyst that is commonly used in PHIP experiments. Short POCs may limit the possible polarization yield as well as applications of PHIP.

Background. Molecular H_2 has four nuclear spin states: one *para*- and three *ortho*-states. p-H_2-enriched H_2 will convert back to *ortho*-H_2 (o-H_2) with a final thermal equilibrium ratio of 3:1 (o-H_2 to p-H_2) at 300 K. The POC can be slow if H_2 is stored appropriately in gaseous phase (on the order of days to weeks [3]), but it is much faster in solution state (hours [4]).

Methods. The POC of dissolved p-H_2 (8–10 bar) was monitored in different solvents with a series of ^{1}H-NMR scans (600 MHz); while p-H_2 shows no NMR signal ($I = 0$), o-H_2 does ($I = 1$). Solutions included H_2O, D_2O and saline solution as well as a D_2O-catalyst solution. The catalyst was Rh-based (a standard PHIP catalyst) and formed by 1,4-bis-[(phenyl-3-propane sulfonate) phosphine]butane disodium salt and bis(norbornadiene)Rh(I) tetrafluoroborate.

Results. In H_2O, D_2O and saline solution, POC times of the order of hours were measured. In samples where air was replaced by N_2 (three freeze-pump-thaw cycles) the POC was slowed significantly, most likely because paramagnetic O_2 was removed. When a Rh catalyst was added to previously degassed D_2O, the POC was strongly shortened; POCs of a few minutes (from 40 min to 5 min) were observed depending on the concentration of the catalyst (from 0.4 mM to 2.0 mM). In D_2O and in D_2O-catalyst solution, prominent HD resonances were observed.

Discussion. The observed POC times in aqueous solutions are promising with respect to possible PHIP and in particular continuous hyperpolarization (cHYP) applications [5]. Future measurements of POC in human blood may clarify, if *in-vivo* cHYP (e.g., after the inhalation of p-H_2) is feasible. It was observed that the investigated catalyst strongly shortens the POC. However, another catalyst was reported to shorten the POC even more – to the order of seconds [6]. Thus, the effect on POC times should be considered when choosing suitable catalysts for PHIP experiments. Additionally, the formation of an HD triplet that was observed for H_2 in D_2O will be further investigated.

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Bias dependence of transient EDMR signals from organic solar cells

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Charge transport in organic semiconductor based solar cells (OSCs) is mediated by localized states that, if singly occupied, become accessible with spin-sensitive techniques such as electron paramagnetic resonance (EPR) and electrically detected magnetic resonance (EDMR) [1,2]. To gain insight into the transport pathways in these cells, we study light-excited and simultaneously detected time-resolved EPR and EDMR signals from fully-processed and encapsulated OSCs. The combination of the two techniques allows a direct connection between photo-induced excitons, charge transfer states and free charge carriers and their contributions to the photocurrent. Furthermore, in changing the biasing conditions (charge carrier injection or extraction), the dynamics of the detected paramagnetic species are affected and hence influence the device current [3].

We present results obtained from bias-dependent transient EPR (trEPR) and transient EDMR (trEDMR) measurements and show that the resonant signals observed at low temperature ($T = 80$ K), attributed to positive polarons in the polymer and negative polarons in the fullerene phase, are involved in different current-influencing processes. Various spin-dependent mechanisms dominate on different time scales after photoinduced exciton generation. The bias dependence of these processes and the dynamics of the corresponding trEDMR signals will be discussed.

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Indirect NMR detection of transient guanosyl radical protonation in neutral aqueous solution

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Basic DNA photochemistry has been subject of numerous investigations, in model systems as well as in isolated and cellular DNA. It is well known, that UV light can interact with DNA either by direct absorption, or via photosensitization by endogenous or exogenous chromophores present in drugs, cosmetic agents, metabolites, etc. Guanine is the main target of one-electron oxidation reactions, as it has the lowest oxidation potential among all DNA components. Upon one-electron oxidation, guanine is converted into a cation radical ($G^{\bullet+}$). The guanine cation radical can deprotonate to form the neutral guanine radical $G(-H)^{\bullet}$, and these two radicals are involved in the subsequent processes of pathological DNA damage.

Recently, Choi *et al.* using time-resolved resonance Raman spectroscopy combined with pulse radiolysis have proposed a new guanine cation radical species $(G^{\bullet+})'$ that results from protonation at the N(7) position of the neutral guanine radical $G(-H)^{\bullet}$ [1]. This work caused some debates, namely Sevilla *et al.* challenged the interpretation of results of Choi *et al.* and noted that the authors did not present strong evidence for the formation of $(G^{\bullet+})'$, since their DFT calculation failed to reproduce the experimental results [2]. From our side, we support the hypothesis proposed by Choi *et al.* and provide evidence for the formation of the new guanine cation radical species $(G^{\bullet+})'$ [3]. Our CIDNP kinetic data, obtained in the photoreaction of guanosine-5-monophosphate (GMP) with the photosensitizer 3,3′,4,4′-tetracarboxy benzophenone (TCBP) in neutral aqueous solution, demonstrate the inversion of the CIDNP sign for both TCBP and GMP on a microsecond timescale.

The independence of CIDNP kinetics on addition of acetate (proton acceptor) and acceleration of CIDNP sign change upon addition of phosphate (proton donor) suggests that the radical transformation responsible for the observed CIDNP kinetics is the protonation of the neutral guanosyl radical at the N(7) position with the formation of cation radical $(G^{\bullet+})'$. From the analysis of pH-dependent CIDNP kinetics, protonation and deprotonation rate constants were determined, which allowed to estimate pK_A of the cation radical $(G^{\bullet+})'$ at 8.2 in D_2O (8.0 in H_2O). The obtained CIDNP data also allows to estimate the g-factor of the N(7)-protonated guanosyl cation radical as being nearly equal to that of the N(1)-protonated guanosyl cation radical.

This work was supported by the Russian Science Foundation (project 15-13-20035).

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Magnetic field effect studies on radical pair reactions in de novo and natural flavoproteins

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Magnetic field effects (MFE) on the photochemistry of *de novo* and natural flavoproteins have been investigated by cavity ring-down spectroscopy (CRDS). The simple, robust, and adaptable design of the *de novo* flavoproteins (flavomaquettes) facilitates detailed MFE studies by circumventing the complexity and diversity of their natural counterparts (cryptochromes), which are believed to play an important role in animal magnetoreception. We have recently demonstrated that photo-induced electron transfer occurs in these flavomaquettes leading to the formation of a spin-correlated radical pair which exhibits MFEs at room temperature [1]. In this work, CRDS was used to detect MFEs on the concentration of transient species with sub-μs time resolution and a sensitivity two orders of magnitude greater than conventional single-pass transient absorption techniques. Detailed insight into the dynamic photo-chemical processes was gained through global analysis and the profound effect of the donor–acceptor distance on the MFE is demonstrated using flavomaquettes with distinctive flavin–tryptophan distances [2].

The innovative approach, applying cavity-enhanced spectroscopy to both natural cryptochromes and purposefully designed artificial flavoproteins, opens up new pathways to explore MFEs in biologically relevant environments.

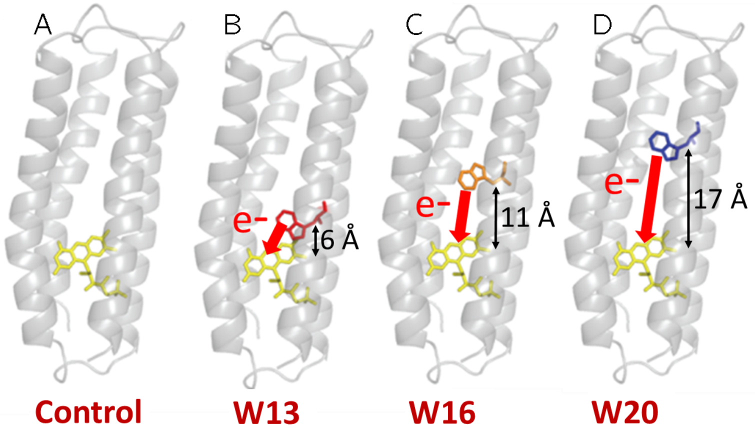

Figure 1: Flavomaquette designs. A: the control with no tryptophan; B, C, and D: designs with tryptophan at increasing distance to the flavin chromophore.

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Author Index

All authors contributing to this conference are listed hereafter alphabetically. The numbers given refer to the actual page numbers where you can find further information, *i.e.*, the abstract of the respective contribution. Please note that bold-face numbers refer to the author being presenting author of the respective contribution.

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