SCM 2013
Bad Hofgastein

SPIN CHEMISTRY MEETING 2013

13th International Symposium on
Spin and Magnetic Field Effects in Chemistry
and Related Phenomena

BOOK OF ABSTRACTS

22 - 26 April, 2013
Bad Hofgastein, Austria

Welcome to the SCM 2013 in Bad Hofgastein / Austria

On behalf of the International Spin Chemistry Committee and the Organizing Committee of SCM 2013, we would like to welcome you all to the 13th Spin Chemistry meeting, being held in Bad Hofgastein / Austria. We are proud to continue the SCM2013 in a series of former meetings, starting in 1991 with the first meeting held in Tomakomai, Hokkaido, Japan, organized by Prof. Y. John I'Haya.

Since more than 20 years, Spin Chemistry remains an exciting area of research including many different interests from various disciplines, like chemistry, biochemistry, physics etc. Spin Chemistry is one of the rare areas combing both experimentalists and theoreticians in an excellent way. We are encouraged in seeing many young scientists presenting highly interesting work.

In 2013 the SCM is located for the first time in Austria, in the valley of Gastein. Bad Hofgastein is a famous tourist place in the summertime for hiking and in the wintertime for skiing. In 2011 the SCM has been in the Netherlands, where Goudsmit and Uhlenbeck postulated the existence of a new intrinsic property of particles that behaved like an angular momentum in 1925. This intrinsic property was later termed spin by Pauli, an Austrian physicist born in Vienna.

Of course, conferences do not just happen. Several people helped us in organizing this meeting. Without their help the meeting would not have been possible. Especially, we would like to thank Peter Hore and Stefan Weber. Their support and contributions were extremely important for us.

We are also grateful for all the sponsors supporting this meeting. They are listed on the following pages.

For wednesday afternoon we organized an excursion to Salzburg including a guided tour through the city of Salzburg. We hope that you will enjoy this trip to the historical Salzburg.

Finally we want to thank all of you for coming. We are delighted to see you in Bad Hofgastein and we hope that you'll find the SCM2013 stimulating and interesting and we are looking forward to exciting lectures with lively discussions and impressive poster contributions.

Günter Grampp
Stephan Landgraf

Previous Meetings

1991 Tomakomai, Japan
1992 Konstanz, Germany
1994 Chicago, USA
1996 Novosibirsk, Russia
1997 Jerusalem, Israel
1999 Emmetten, Switzerland
2001 Tokyo, Japan
2003 Chapel Hill, USA
2005 Oxford, UK
2007 San Servolo, Italy
2009 St. Catharines, Canada
2011 Noordwijk, The Netherlands

Present Meeting

Kongresszentrum Bad Hofgastein
c/o Kur- und Tourismusverband
Tauernplatz 1
5630 Bad Hofgastein
Austria
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Program

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10h15 – 10h45	Conference photo & Coffee break	
10h45 – 11h15	IT2 **E. Schleicher**, Freiburg, DE « Radicals and Radical Pair in Blue Light Photoreceptors »	Chair : Hore
11h15 – 11h45	IT3 **K. Maeda**, Oxford, UK « Reaction Kinetics and Magnetoreception in Chryptochromes and Photolyase »	
11h45 – 12h10	IT4 **J.B. Phillips**, Blacksburg, US « Behavioral and Neural Mechanisms Mediating Light-Dependent Magnetoreception »	
12h10 – 12h35	CT1 **R. Carmieli**, Evanston, US « DNA Spin Switches Based on Controlling Charge Transport »	

15h00 – 15h30	IT5 **S.R. Mackenzie**, Oxford, UK « Advances in the Optical Detection of Magnetic Field Effects in Biological Systems »	Chair : Naaman
15h30 – 16h00	IT6 **A.R. Jones**, Manchester, UK « Are Cryptochromes Magnetic-Sensors in Animals or Simply Necessary for Magnetoreception ? »	
16h00 – 16h30	IT7 **C.R. Timmel**, Oxford, UK « From Radiofrequency to Microwave Fields : Exploring the Recombination Kinetics of a Photo-Induced Radical Pair »	
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18h25 – 18h55	IT10 **J. Matysik**, Leipzig, DE « Photo-CIDNP MAS NMR : New Developments »	
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20h – open end	Poster session (odd numbers present)	

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Abstracts

Spin and Chirality from Spintronics to Biology

Ron Naaman

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Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. Hence, most of the development in spintronics is currently based on inorganic materials. In several studies, however, it was found that chiral organic molecules can act as spin filter for photoelectrons transmission, in electron transfer, and in electron transport [1-4].

Results will be presented from several recent experiments. Among others, experiments on electron transmission through biological membranes that contain proteins and electron transfer from a donor to a surface through chiral self-assembled molecules. A new type of spintronics devices will be described and implications related to biology will be discussed.

[1] Ray, K.; Ananthavel, S.P.; Waldeck, D.H.; Naaman, R. Asymmetric scattering of polarized electrons by organized organic films made of chiral molecules. *Science* **1999**, *283*, 814.

[2] Göhler, B.; Hamelbeck, V.; Markus, T.Z.; Kettner, M.; Hanne, G.F.; Vager, Z.; Naaman, R.; Zacharias, H. Spin Selectivity in Electron Transmission Through Self-Assembled Monolayers of dsDNA. *Science* **2011**, *331*, 894-897.

[3] Xie, Z.; Markus, T.Z.; Cohen, S.R.; Vager, Z.; Gutierrez, R.; Naaman, R. Spin specific electron conduction through DNA oligomers. *Nano Letters* **2011**, *11*, 4652-4655.

[4] Naaman, R.; Waldeck, D.H. The Chiral Induced Spin Selectivity Effect. *J. Phys. Chem. Lett.* **2012**, *3*, 2178-2187.

Towards spatially resolved MFE measurements in biological systems

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An important question addressed by spin chemists has been that of whether magnetic fields can exert measurable influences in biology. Indeed the observation of such effects has proved quite controversial due to the difficulty of reproducing observed effects across different laboratories. The most promising target for the observation of robust and significant magnetic field effects in biology has come from the attempt to understand the ability of many species to navigate in the earth's magnetic field. Much progress has been made since 2000, when Ritz *et al.* reinvigorated Shulten's original 1978 proposal of the radical pair as a magnetic compass[1]. This work identified the eye as the likely location of the sensor, and a group of newly discovered proteins, called cryptochromes, as the likely source of the radical pair. From one direction, spin chemists have tried to study both model reactions and simplified systems involving cryptochromes and related photolyases *in vitro*[2]. From the other direction, biologists have increasingly improved our understanding of the nature of the magneto-sensing ability and the physical location and characteristics of the sensing apparatus[3]. These two communities have yet to meet in the middle and this research aims at trying to build a bridge between them.

The ultimate goal of the research is to study the effects of external magnetic fields on biological RPs within real biological structures – cells in the first instance. To do so requires construction of a microscope that can directly observe the species involved in spin-selective reactions within the subcellular structures in which they are found in nature. Furthermore, it must be able to discern small changes in their concentrations induced by the presence of magnetic fields. We present here our preliminary results in developing such an experimental approach. Although we focus our efforts on the study of flavoproteins in general and cryptochromes in particular, we aim at developing general experimental methods to observe magnetic field effects on reactions within microstructures in a spatially-resolved manner, which have a wide range of other applications of interest to the spin chemistry community.

[1] Ritz *et al*, *Biophys. J.* **2000**, *78*, 707-718; . Schulten, *et al*, *Z. Phys. Chem.* **1978** NF111:1–5.

[2] See recently, Maeda *et al*, *PNAS* **2012,** 109, 4774-4779.

[3] See, for example, Liedvogel M., Mouritsen H. J., *Roy. Soc. Interface* **2010**, 7:S147–S162.

Radicals and Radical Pair in Blue Light Photoreceptors

Erik Schleicher[1], Till Biskup[1], Bernd Paulus[1], Csaba Bajzath[1], Richard Brosi[2], Robert Bittl[2], and Stefan Weber[1]

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Three different classes of flavin-containing blue-light photoreceptors, namely LOV domains, BLUF domains and cryptochromes, are known to date. Although these proteins share the same flavin chromophore, their primary photoreactions differ significantly. Electron-transfer reactions are supposed to be involved an all three classes of blue-light photoreceptors, therefore electron paramagnetic resonance (EPR) methods in all flavors are particularly suited to identify and characterize (short-lived) paramagnetic intermediates (radicals, radical pairs and triplet states) [1] even in *in vivo* systems [2].

In this contribution, we describe the identification of key amino acids for efficient electron transfer in cryptochromes (and photolyases), and the finding of a secondary electron transfer if conserved amino acids of the primary electron transfer pathway are blocked [3]. Moreover, we could demonstrate that the kinetics of this photo-induced electron transfer reaction is magnetically sensitive, which argues that cryptochrome is fit for purpose as a magnetoreceptor [4].

[1] Schleicher, E. and Weber, S. *Topics in Current Chemistry*, **2012**, *321*, 41-66.

[2] Banerjee, R. ; Schleicher, E. ; Meier, S. ; Muñoz Viana, R. ; Pokorny, R. ; Ahmad, M. ; Bittl, R.; Batschauer, A. *J. Biol Chem*. **2007**, *282*, 14916-14922.

[3] Biskup, T. ; Paulus, B. ; Okafuji, A. ; Hitomi, K. ; Getzoff, E. D. ; Weber, S. ; Schleicher, E. *J. Biol Chem*. **2013**, *in press.*

[4] Henbest, K. B. ; Maeda, K. ; Hore, P. J. ; Joshi, M. ; Bacher, A. ; Bittl, R. ; Weber, S. ; Timmel, C. R. ; Schleicher, E. *Proc Natl Acad Sci USA*. **2008**, *105*, 14395-14399.

Reaction Kinetics and Magnetoreception in cryptochromes and photolyase.

K. Maeda[1], J. G. Storey[1], K. B. Henbest[1], S. R. T. Neil[2], H. J. Hogben[2], T. Biskup[3],
K. Hitomi[4], E. D. Getzoff[4], M. Ahmad[5], E. Schleicher[3], S. Weber[3], S. R. Mackenzie[2],
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[4]Department of Molecular Biology and the Skaggs Institute for Chemical Biology,
The Scripps Research Institute.
[5]Université Paris VI

Blue-light photo-receptor proteins, in particular cryptochromes, have received attention recently as the most likely magnetoreceptors in the avian magnetic compass and as potential mediators of biological effects of extremely low frequency electromagnetic fields. Here, we describe recent *in vitro* spectroscopic studies of the magnetic field effects (MFEs) on photochemically formed radicals in cryptochrome/photolyase family proteins, focusing on radical pair (RP) kinetics optimal for magnetoreception.

1) MFEs were observed for *Arabidopsis thaliana* cryptochrome (*At*-CRY) and *E. coli* photolyase (*Ec*-PL) using transient absorption (TA) laser flash photolysis [1]. In the photoreaction of *Ec*-PL, we noted the transformation of [$\mathrm{FAD}^{\bullet-}$ $\mathrm{TrpH}^{\bullet+}$] (referred to as RP1) into [$\mathrm{FAD}^{\bullet-}$ $\mathrm{Trp}^{\bullet}$] (RP2). RP1 is crucial for MFEs because it has active spin-selective back-electron transfer and RP2 lives long enough to preserve the MFE.

2) Recently we have developed a cavity-based method for measuring MFEs: cavity ring-down (CRD) spectroscopy [2]. The powerful capabilities of this technique, which includes sub-microsecond time-resolution, high sensitivity and small (μL) sample volumes, have the potential to allow studies of the magnetic sensitivity of highly dilute biomolecular samples.

3) The combined technique of CRD spectroscopy and nanosecond magnetic field switching (MFS) was applied to *Xenopus laevis* DASH-cryptochrome (*Xl*-CRY) [3]. CRD spectroscopy and MFS showed a much shorter lifetime (~100 ns) for RP1 than in *At*-CRY or *Ec*-PL. From a precise analysis, the singlet recombination rate constant (k_S) was found to be about 40 times faster than that of *Ec*-PL. This result indicates the remarkably wide tuning range of the reaction kinetics in different cryptochrome/photolyase proteins.

This work was funded in part by the EMF Biological Research Trust and DARPA.

[1] Maeda, K.; Robinson, A.J.; et al. *Proc. Natl. Acad. Sci. USA* **2012,** *109,* 4774-4779.
[2] Maeda, K.; Neil, S.R.T.; et al. *J. Am. Chem. Soc.* **2011,** *133,* 17807-17815.
[3] Biskup, T.; et al. *Ang. Chem. Int. Ed. Engl.* **2008,** *47,* 1-5.

Behavioral and neural mechanisms mediating light-dependent magnetoreception

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Magnetic compass orientation by animals as diverse as flies, amphibians, birds, and epigeic rodents (mice, rats) exhibits properties consistent with a RPM. However, virtually nothing is known about the primary receptors that mediate these responses, or the nature of the input that these receptors provide to the central nervous system. In this talk I'll discuss evidence (1) that the putative RPM generates a complex pattern of response unlike that expected from (e.g.) a magnetite-based mechanism, (2) that this response is disrupted by background levels of radio frequency interference found in typical laboratory environments, and (3) that, in birds and mammals, magnetic input from the RPM plays a more fundamental and important role in spatial behavior and cognition than that of providing simple directional ('compass') information.

DNA Spin Switches Based on Controlling Charge Transport

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Synthetic DNA hairpins with chromophore linkers have provided a versatile system for the investigation of photoinduced charge-transfer processes in B-form DNA [1,2]. The synthetic strategy for hairpin synthesis has now been used to prepare a dichormophoric hairpin with a controlled base sequences for the purpose of acting as a photo molecular switch. Here we show for the first time that although DNA may not be a good molecular wire, this actually makes it a good tunable system to serve as a molecular quantum switch where by selective wavelength excitation a singlet initiated radical-pair or triplet initiated radical-pair are being formed and as a results different quantum information/coherences can be transferred based on the different population of the singlet-triplet sublevels.

[1] Zeidan, T.A.; Carmieli, R.; Kelly, R.F.; Lewis, F.D.; Wasielewski M.R. Charge-Transfer and Spin Dynamics in DNA Hairpin Conjugates with Perylenediimide as a Base-Pair Surrogate. *J. Am. Chem. Soc.* **2008,** *130*, 13945-13955.

[2] Carmieli, R.; Smeigh, A.L; Mickley-Conron, S.M.; Thazhathveetil, A.K.; Fuki, M.; Kobori, K.; Lewis, F.D.; Wasielewski M.R. Structure and Dynamics of Photogenerated Triplet Radical Ion Pairs in DNA Hairpin Conjugates with Anthraquinone End Caps. *J. Am. Chem. Soc.* **2012**, *134*, 11251-11260.

Advances in the optical detection of magnetic field effects in biological systems

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We report here on the application of novel optical cavity-based spectroscopic techniques to the study of magnetic field effects in biological systems involving spin-correlated radical pairs. These methodologies, adaptations of similar techniques developed for trace detection in the gas-phase, offer significant benefits in sensitivity over single-pass experiments. These gains are sufficient to permit studies of MFEs not just in model systems but also in real biological samples such as cryptochromes, which are postulated to play a key role in animal magnetosensitivity.

We have developed condensed phase variants of cavity ring-down spectroscopy (CRDS) and cavity enhanced absorption spectroscopy (CEAS) both of which will be described. Particular focus, however, will be given to broadband CEAS which, as we will demonstrate, provides full (visible) spectral information and magnetic field sensitivity simultaneously. Examples presented will include flavin-based model systems as well as cryptochromes.

In addition to the optical cavity-based experiments we will describe parallel developments in the fluorescence detection of MFEs. Where applicable, fluorescence represents a zero background detection method which can enhance the sensitivity well beyond direct absorption techniques.

Are Cryptochromes Magnetic-Sensors in Animals or Simply Necessary for Magnetoreception?

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Cryptochromes are now positioned as the most likely biomolecular candidate to act as a light-dependent chemical compass in the radical pair model of animal magnetoreception. An electron transfer cascade is proposed to proceed along a conserved triad of tryptophan residues (Trp-triad) to a fully oxidised, photoexcited flavin, thus producing a magnetically-sensitive flavin semiquinone / tryptophanyl radical pair [1]. This mechanism appears to facilitate photoreduction and magnetic-sensitivity *in vitro*. However, there are *in vivo* data that suggest although cryptochromes are necessary for photo- and magnetoreception, the Trp-triad is not required in either case *e.g.* [2-3].

In 2011 an X-ray crystal structure of full-length *Drosophila* cryptochrome was published that proposed an alternative electron transfer pathway [4]. A different tryptophan residue from the C-terminal tail (Trp536) was presented to be within ~4.7 Å of the FAD. After close scrutiny of the structure in [4] we discovered a number of problems that have significant implications for this proposition. A rebuild from the original data, which has been accepted by the authors of [4] as a more accurate structure [5], indicates that the sequence register of the C-terminal tail is displaced by two residues. The effect is that Trp536 from the original structure is replaced by Phe534, with Trp536 now ~ 9.6 Å from the FAD with His378 between the two. The implications of this will be discussed within the context of cryptochrome as a magnetic-sensing molecule in animals.

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From Radiofrequency to Microwave Fields: Exploring the Recombination Kinetics of a Photo-Induced Radical Pair

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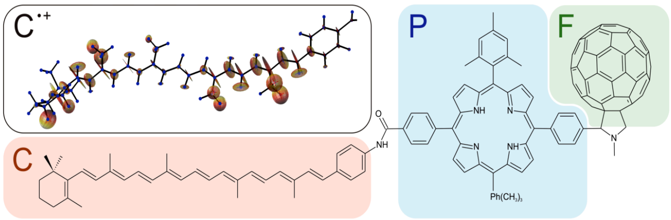

Figure 1 Structure of the CPF triad and a representation of the anisotropic hyperfine interactions of the carotenoid radical cation (inset).

Recent experiments on a carotenoid-porphyrin-fullerene (CPF) compound have established the principle that a photochemical reaction could form the basis of the magnetic compass sensor of migratory birds [1]. Here, the effects of static, radiofrequency and microwave magnetic fields on the spin-selective recombination reactions of the radical pairs derived from a number of related triad systems are studied using transient absorption and time-resolved EPR spectroscopies. Estimates of the charge recombination rates are obtained and related to the size of the field effects observed. The anisotropy of the magnetic field effects in these systems is studied as a function of both solvent temperature and magnetic field strength. Density Functional Theory calculations accompany the experimental investigations and predict magnetic parameters which dictate the field effect characteristics such as the radicals‘ hyperfine coupling tensors.

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Magnetoreception in Drosophila melanogaster

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It has been previously reported that circadian locomotor activity of Drosophila melanogaster can be modified by a static magnetic field (MF) under blue light (465 nm), matching the action spectrum of CRYPTOCHROME (CRY), the dedicated blue-light circadian photoreceptor. However, these behavioural effects are extremely weak and are open to alternative interpretations. By using the Schuderer Apparatus, we have confirmed, albeit with rather different results, that a low frequency AC-EMF along with a Static Field exposure does affect circadian behaviour in the fruitfly. Furthermore, using different paradigms, EMF appears to consistently and robustly disrupt CRY function, thereby indirectly supporting the Radical Pair Theory.

Photoinduced Radical Pairs in Cryptochromes: Possible Candidates for the Magnetic Compass of Migratory Birds

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Over the last decade a mounting body of evidence has accumulated for different animal species being capable to sense the Earth magnetic field and to use this information to orient themselves, the most prominent being migratory birds, whereas the underlying mechanism remains unknown. One possibility, a radical pair (RP) based compass, was first theoretically proposed by Schulten and coworkers in 1978, but it was not until the discovery of the cryptochromes (Cry) that this hypothesis got revived, this time with a candidate molecule.

Using time-resolved EPR (TREPR) on a Cry from *Xenopus laevis*, we could for the first time demonstrate that Crys indeed form spin-correlated RPs between FAD and Trp upon blue-light illumination [1], a necessary but not sufficient prerequisite for being a magnetoreceptor. Additionally, we assigned the RP partners and showed that the magnetic coupling parameters of these RPs are in favour of their proposed role as a compass. Using a multi-frequency TREPR approach (X- and Q-band) we could unequivocally demonstrate the formed spin-correlated RPs to originate from a pure singlet-precursor state [2].

Turning to another Cry, from *Synechocystis* sp., revealed a striking diversity in electron transfer (ET) pathways in Crys [3]. Finally, we could show that blocking the ET pathway in *X. laevis* Cry at the first or second position (TrpA or TrpB) leads to another alternative ET involving two tyrosines (Tyr). Here, we could show that TREPR even at X-band can clearly distinguish between FAD-Trp and FAD-Tyr RPs. Taken together, these results reveal an unexpected diversity in ET pathways in Crys and show that EPR is clearly suited to investigating it.

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Quantum coherence and quantum control in radical pair mechanism of magnetoreception

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It is known that more than 50 species use the Earth's magnetic field for orientation and navigation. Intensive studies particularly behavior experiments with birds have provided supporting evidences for a mechanism based on magnetically sensitive free radical reactions. However, the fundamental question of whether and how quantum coherence plays an essential role in such a chemical compass model of avian magnetoreception or whether it is merely a by-product arising from the underlying system dynamics yet remains controversial. In this talk, I will present our studies on the role of different key ingredients, such as hyperfine couplings, quantum coherehce and decoherence, which are responsible for the high sensitivity of a chemical compass. We also demonstrate how one can gain new insights into the radical pair mechanism and design a biomimetic weak magnetic field sensor with quantum control techniques.

Photo-CIDNP MAS NMR: New Developments

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Photo-CIDNP MAS NMR has been developed to a standard analytical method for the analysis of photosynthetic radical pairs [1]. The understanding of the mechanism of photo-CIDNP production allows for detailed studies on reaction centers (RCs) for example of purple bacteria [2,3], heliobacteria [4], and algae and plants [5]. In particular, the reconstruction oft he donor triplet state of the Special pair donor of RCs of *Rhodobacter sphaeroides* allows reconstruction of the excited state and the mechanism of directional electron transfer [3].

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Dynamics of Nuclear Singlets and Triplets

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Many effects in spin chemistry are related to the dynamics of electronic singlet and triplet states, and their interconversion. Related effects exist for nuclear spins too. For example, parahydrogen is a nuclear singlet state and usually interconverts very slowly with the nuclear triplet state of orthohydrogen. We have been studying the dynamics of nuclear singlet-triplet interconversion in a variety of species, including hydrogen and water trapped inside fullerenes at low temperatures, as well as room temperature solutions containing nuclear spin-1/2 pairs in slightly inequivalent sites. We have shown that it is possible to repeatedly convert long-lived nuclear singlet order into nuclear magnetization, and back again, over a timescale of tens of minutes.

Some of the following topics will be presented:

- Ortho-para conversion of H_2O inside C_{60} fullerene: Is o/p conversion autocatalyzed?
- Ortho-H_2 inside C_{70} fullerene: A (sort of) liquid crystal at 4 Kelvin?
- Inducing singlet-triplet conversion by ^{18}O substitution
- Maintaining ^{13}C polarization as singlet order in solution for 30 minutes
- Mechanisms of nuclear singlet-triplet conversion in solution. Quantum chemistry and molecular dynamics studies. The return of spin-rotation as a nuclear relaxation mechanism?

Magnetic field effect on two-dimensional diffusion-controlled radical recombination

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Free radicals play an important role in many numbers of chemical and biological processes. For instance, lipid peroxidation chain reaction, which is responsible for the destruction of cellular membranes, proceeds through few radical recombination steps. In view of the importance of lipid peroxidation the theoretical description of radical recombination in two-dimensional lipid bilayers taking into account the spin-selectivity of the reaction becomes particularly topical. The kinetic equation for diffusion-influenced bimolecular reactions in two-dimensional space is well-known [1-2]. However, this equation has been derived neglecting the spin-selective character of the radical recombination reaction. The spin-selective recombination of radicals with a uniform spatial distribution has been treated theoretically only in the three-dimensional case [3-4].

We present analytical and numerical results of calculation of magnetic field effect in two-dimensional radical recombination. The effect of singlet-triplet mixing of spin levels of encounter radicals by an external magnetic field and by hyperfine couplings, electron spin relaxation is considered. Analytical expressions have been obtained for the rate coefficient of spin-selective recombination of radicals in one, two, and three dimensions. The size of possible magnetic field effects on recombination of lipid radicals on the cellular membrane surface has been estimated.

This work was supported by RFBR (grants 11-03-00356, 11-03-00296, 12-03-33082), SB RAS (interdisciplinary project No. 71), Division of Chemistry and Material Science RAS (project 5.1.1) and program P-220 of the Government of RF (grant 11.G34.31.0045).

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Electron spin relaxation of NO radical in liquid solution

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The small, linear inorganic radicals NO and O_2^- exhibit important functions in cell biology. They have, however, not yet been detected by ESR under in vivo conditions because of their extremely short electron spin relaxation times. Nevertheless a spin chemical magnetic field effect has been claimed for the recombination of these radicals when forming the peroxy nitrite anion.[1] In high magnetic fields, such magnetic spin effects are possible because chemical reaction and Zeeman mixing of the radical pair's singlet and triplet (T_0) state are fast enough to compete with spin relaxation. A tentative theory of this effect was based on the assumption of spin-rotational relaxation in the NO radical as the dominant contribution and its description by the standard equation of spin-rotational relaxation [2]:

$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{\overline{\delta g^2}}{9}\frac{1}{\tau_c} \text{ with } \overline{\delta g^2}=\left(g_{\|}-g_e\right)^2+2\left(g_{\perp}-g_e\right)^2$$

where τ_c denotes the orientational correlation time of the radical. The equation is valid only for g-tensors not too different from the value g_e of the free electron and for g-tensor axes fixed in the molecular frame. Both of these assumptions are questionable for NO in liquid water. Its g-tensor and the splitting of its two lowest Kramers doublets are determined by the electrostatic ligand field interaction with the surrounding water molecules. It is a rapidly changing interaction both in strength and direction. We present an in-depth analysis of the time dependent perturbations controlling the relaxation of the NO radical's magnetic moment under such conditions. Our analysis is based on a quantum mechanical (Car-Parrinello) MD calculation for NO surrounded by water molecules, from which the correlation functions of the direction and strength of the ligand field splitting are obtained. The effect of the fluctuating interactions on the magnetic moment is calculated by explicit numerical time integration of the equation of motion of the effective spin.

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Spin Effects in the Reaction of Electron Transfer to Nitroxide Radicals

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This work presents a study of spin effects in reactions between excess electrons and nitroxide radicals in liquid alkanes. To perform this, a little-exploited experimental approach, which is based on the analysis of the kinetics curves of the fluorescence intensity decays from irradiated solutions of studied compounds, has been used. The response of the kinetic curves to external fields, electric or magnetic, as well as to additional charge acceptors allows one to gain information about geminate radical ions regarding their transport properties [1], paramagnetic characteristics [2], mono- and bimolecular reactions of charge transfer [3], respectively.

In this work, a correlation between the spin selective [4] scavenging of excess electrons by nitroxide radicals and the spin coherence in the surviving geminate pairs (electron/radical cation) has been studied. It has been found that the rates of both the scavenging and the spin decoherence are equal in the absence of spin exchange interaction.

The present work is supported by RFBR (grant 11-03-01003-a) and the Program of Leading Scientific Schools (grant NS-2272.2012.3).

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Intramolecular electron transfer in chiral linked systems.

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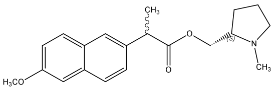
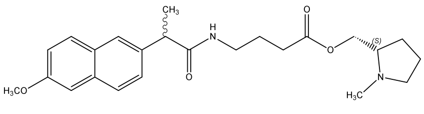
The study of photoinduced intramolecular electron transfer (PET) in the linked systems is actual due to the presence of this stage in important nature processes such as photosynthesis, the reaction of certain enzymes (oxygenases, dioxygenase), and etc. PET attracts additional attention in the presence of chiral centers in the systems under study. Usually, chiral isomers have equal chemical properties, but it is not always the truth. But the reference data devoted to the influence of chirality on the chemical reactivity is scarce and to the same degree contradictory, because existing examples apply to the very complex reactions. In this context the recent report about observation of the difference in the rate of PET between diastereomers of dyads [1], as we believe, is very promising. This report is devoted to studying PET in chiral dyads: [R, S]-((S)-1-methylpyrrolidin-2-yl)methyl 2-(6-methoxynaphthalen-2-yl)propanoate**(I),** ((S)-1-methylpyrrolidin-2-yl) methyl 4-[R, S] -2-(6-methoxynaphtalen-2-yl)propanamido)butanoate**(II)**, (1R,3S)-((S)-1-methylpyrrolidin-2-yl) methyl 3-([R, S]-2-(6-methoxynaphthalen-2-yl)propanamido)cyclopentanecarboxylate**(III)**.



(I)



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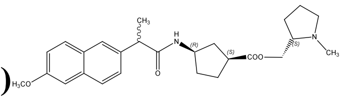

(III)

The investigation has been done by two methods: chemical induced dynamic nuclear polarization and fluorescence spectroscopy in solvents with different polarity.

It has been shown that quenching process involves not only PET that leads to ion-biradical formation but singlet exciplex, which is in a fast equilibrium with PET. It has been suggested that exciplex is the very place where stereodifferentiation is created.

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Supramolecular Control of Spin-Dependent Electron Transfer Dynamics in Micellar Supercages as Studied by Magnetic Field Effects

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Photo-generated radical (ion) pairs in micellar cages are one of the most classical and well-studied systems in the field of spin chemistry. Numbers of experimental and theoretical reports have been published on the magnetic field effects (MFEs) and spin polarized EPR spectra of long-lived caged radical pairs.[1] These studies have contributed to clarification of characteristic dynamics and electronic interactions of the caged radical pairs, but following questions are still not clear as of now though they are crucial for understanding nature of membrane-like environments as electron transport media and for development of artificial photon-energy conversion systems using cheap surfactants; 1) Mechanisms of spin selectivity of long-lived charge separation and the reason of rareness of singlet-born long-lived systems and 2) Role of hydrogen-bonded water network on the long-distance electron transport.

In this talk, we report on electron transfer (ET) in a novel supramolecular cage constructed by an amphiphilic viologen acceptor and nonionic TX-100 surfactant molecules, whose cage size is controlled by the acceptor concentration. Two ET systems have been studied. In the former system, long-lived radical pairs are generated from both of excited singlet and triplet states of a hydrophobic polyaromatic molecule, which show size dependent spin selectivity (Figure 1a). The second system is sequential ET triads utilizing the alkyl phenoxy moiety of TX-100 as a donor combined with flavins and the violoen as primary and secondary acceptors, respectively(Figure 1 b).[2] Details on spin-dependent ET dynamics in these systems studied by transient absorption detected MFE, time-resolved fluorescence and dynamic light scattering will be discussed.

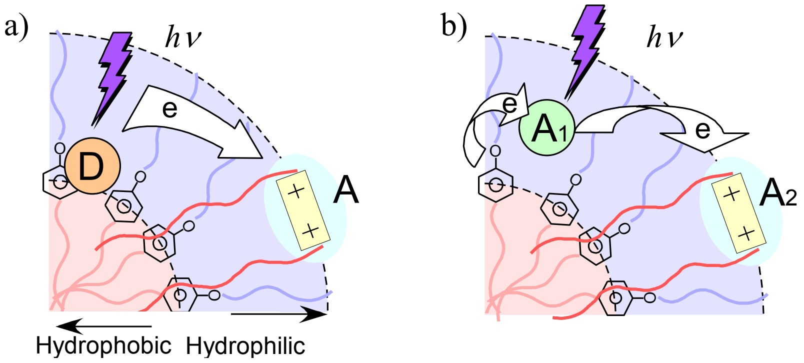

Figure 1. Schematic illustrations of phase-separated donor-acceptor systems in this study.

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Theoretical insights into chemical magnetoreception: past, present and future

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Creatures as varied as mammals, fish, insects, reptiles, and migratory birds have an intriguing 'sixth' sense that allows them to navigate using the Earth's intrinsic magnetic field. A photoreceptor, cryptochrome, has been suggested to endow birds with magnetoreceptive abilities as the protein has been shown to exhibit the biophysical properties required for an animal magnetoreceptor to operate properly. Cryptochromes are flavoprotein photoreceptors originally identified in *Arabidopsis thaliana*, where they play key role in growth and development. Subsequently discovered in *prokaryotes*, *archaea*, and *eukaryotes*, cryptochromes were shown to be involved in the animal circadian rhythms. The unique biological function of cryptochromes arises due to the very special photoactivation reaction occurring in the proteins: exposure to blue light results in the reduction of flavin pigments that are bound by the cryptochromes, which leads to the formation of a spin-entangled pair of radicals, the so-called radical-pairs.

However, despite decades of research, it is still unclear if cryptochrome is hosting the key radical pair needed for chemical magnetoreception, mainly because the molecular reactions of the radical pair in cryptochrome are not fully resolved yet. Using *ab initio* quantum chemistry we partially filled in this missing gap and investigated cryptochrome photoactivation. Our study focused on transient state formation in cryptochrome's post-light-activation, thereby, answering how the radical pair in cryptochrome is formed and what its fate may be. The proposed reaction provides the foundation for further studies of magnetoreceptive properties of cryptochrome, as it accounts for intermediate states in the protein which can be magnetic field sensitive.

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Theory of pulsed reaction yield detected magnetic resonance

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We have developed the theory of pulsed Reaction Yield Detected Magnetic Resonance (RYDMR) and suggest analogues of the main EPR pulse sequences in the case of non-selective mw-pulses. We have used refocusing of the zero-quantum coherences in the Radical Pair (RP) and formulated a criterion for observing spin echoes in RYDMR where not the spin magnetization but the singlet state population is used as an observable. The primary echo sequence has been studied, which can be extended to an analogue of the Carr-Purcell sequence with multiple echoes coming from subsequent pulses. We have suggested an Electron Spin Echo Envelope Modulation (ESEEM) pulse sequence for observing modulations caused by the electronic spin-spin interactions that can be used to probe the distance between the radicals in the RP. Finally, analogues of the stimulated echo sequence and the Mims ENDOR (Electron Nuclear Double Resonance) sequence have been proposed. The treatment was also extended to RYDMR with selective pulses; in this case we considered refocusing of both zero-quantum and single-quantum coherences. This enables extending the capabilities of pulsed RYDMR even further, for instance, by using pulse sequences of the ELDOR (Electron Electron Double Resonance) type, which can be used for measuring electron-electron interactions in the RP.

The theoretical results can be used to extend the scope of RYDMR spectroscopy and fully exploit its potential. In combination with the high sensitivity of RYDMR, techniques using pulsed methods can provide new attractive options for more detailed study of structure, dynamics and reactivity of the short-lived RPs and properties of paramagnetic charge carriers in organic semiconductors.

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Manifestation of interparticle interaction in magnetic field effects on diffusion-assisted spin selective reactions

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Strong attractive interaction between particles is known to significantly affect the kinetics of diffusion assisted condensed phase physico-chemical processes (both geminate and bulk) [1]. This effect mainly results from efficient caging of reacting particles in the presence of the interaction. The important information on specific features of the interaction affected reaction kinetics can be obtained by investigating magnetic field effects (MFEs) because the MFE amplitudes and their dependences on parameters of spin dependent interactions appear to be fairly sensitive to these specific features.

This work concerns the theoretical study (within the stochastic Liouville equation approach) of the effect of interparticle-attraction-induced caging on MFEs. The rigorous analytical analysis shows, in particular, that in the presence of the cage effect the short time reaction kinetics is quite accurately described by simple first order kinetic equations. As for the long time stage of the kinetics (at times longer than the cage life time), it is strongly non-exponential and is determined by reaction of freely diffusing particles escaped from the cage [2]. The relative significance of both kinetic stages depends on the depth of the attraction potential. Naturally, the attraction-induced cage effect on reaction kinetics and MFEs most significantly manifest themselves in recombination of ion radical pairs, which is strongly influenced by the Coulomb interaction.

The proposed analysis enables one to describe the non-analytic dependence of some MFEs on the magnetic field B: ($\sim\sqrt{B}$), for example, MFE on conductivity of organic semiconductors [3]. This dependence is attributed to the contribution of recombination of freely diffusing (charged) radicals escaped from the attractive potential well.

The analysis also demonstrates the dependence of specific features of the considered attraction affected (cage affected) reaction kinetics and MFEs on the space dimensionality and on the external field.

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Photo- and Spin Chemical Study on Inclusion Compounds

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Host molecules of inclusion compounds such as cyclodextrines (CDs) and calixarenes 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 interaction in the complex is also known as a simplified model of biological enzymes. For photochemists, 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 nano-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 time-resolved EPR (tr-EPR) investigations of the excited triplet state of aromatic compounds and triplet radical pairs included in CDs have been reported at low temperature [1~3]. These reports showed specific inside environment of CDs depending upon their bore size. According to the photochemical point of view, a tr-EPR observation of aqueous CD solution [4,5] is also a powerful way to investigate the chemical reaction and molecular and/or spin dynamics which are quite interesting along with the inclusion conditions. In the present report, recent tr-EPR study on the photochemistry of aqueous solution of several sulfonated anthraquinones included in CDs and the contribution of the position of a SO_3^- group on anthraquinones to the reaction and dynamics are presented and discussed.

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Magnetic Modulation of Room Temperature Phosphorescence

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Control over dynamics of excited states of molecules is of fundamental importance for utilization of these states in all areas of technology. We are exploring the possibility of controlling formation of phosphorescent triplet states by influencing spin dynamics in radical pairs, formed as a result of photoinduced electron transfer (PET). Our end goal is to utilize these states in a new form of molecular imaging, combining optical and magnetic modalities. Studies of electron and energy transfer dynamics in series of donor-acceptor systems, comprising phosphorescent platinum (II) porphyrins (PtP) and rhodamine B (RhB) derivatives will be presented. In one series, phosphorescent triplet states of PtPs are generated by way of photo-excitation of RhB, followed by PET with formation of singlet radical pair, radical pair intersystem crossing, and subsequent radical pair recombination [1]. Unique properties of these systems allowed observation of electron transfer and triplet-triplet energy transfer in the same series molecules, enabling direct comparison between the distance attenuation factors of these two closely related phenomena. Using another series of molecules we demonstrate for the first time that visible room-temperature phosphorescence, resulting from direct spin-allowed transition of PtP, can be modulated by weak magnetic fields (<1T) [2]. Furthermore, similar effect has been observed upon diffusinal encounters of phosphorescent metalloporphyrins with dark lectron transfer quenchers. This demonstration opens up new possibilities for utilization of emissive triplet states in imaging.

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Photodynamic Therapy, Toils and Troubles: Problems Solved With Tiny Bubbles

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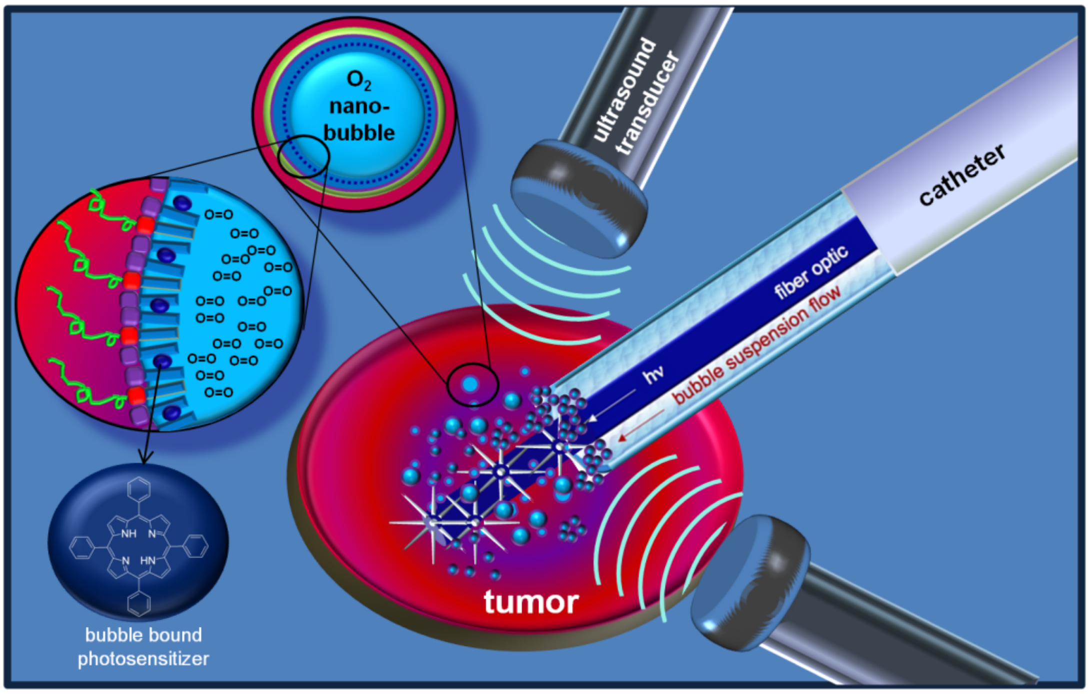

Photodynamic therapy (PDT) uses visible light, a sensitizer such as a porphyrin, and oxygen gas to create singlet oxygen ($^1O_2$), a reactive oxygen species that can kill cancer cells. Historically, PDT has remained a non-invasive treatment, using red light and ambient oxygen after intravenous administration of the sensitizer. Here we describe an invasive methodology for PDT that uses highly efficient blue light coupled with localized microbubble-based delivery of sensitizer and oxygen. Lipid-based air bubbles with stabilizers are administered via a teflon or stainless steel catheter containing a concentrically placed fiber-optic cable. Ultrasound transducers are used to acoustically image the catheter and bubbles. Ultrasound can also be used to manipulate the bubbles (moving or popping). The kinetics and topology of singlet oxygen production can be studied quantitatively by reacting secondary amines with the $^1O_2$ to produce stable nitroxide radicals, detectable at μM concentrations by electron paramagnetic resonance (EPR) spectroscopy. The sensitivity of nitroxide EPR spectra to local order in heterogeneous structures such as bubbles, vesicles, and micelles will also be presented and discussed.

Spin Coherence Transfer by Optical Excitation of Spin-Correlated Radical Pairs

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Controlling the spin dynamics of complex multi-spin molecular systems is a major goal in spintronics and quantum information processing. Fast photo-initiated electron transfer within covalently-linked organic donor-acceptor molecules having specific donor-acceptor (D-A) distances and orientations results in formation of spin-entangled electron-hole pairs (i.e. radical ion pairs, RPs) having well-defined initial spin configurations, while time-resolved electron paramagnetic resonance (TREPR) techniques provide an important means of manipulating and controlling these coherent spin states. Organic RPs display coherent spin motion for up to ~100 ns, which makes it possible that this coherence may provide the basis for new quantum information processing strategies based on organic molecules.

In this talk we will describe photoexcitation of the electron donor (D) within a linear, covalent donor-acceptor-acceptor molecule (D-A_1-A_2) in which $A_1 = A_2$ results in sub-nanosecond formation of a spin-coherent singlet radical ion pair state, $^1(D^{+\bullet}$-$A_1^{-\bullet}$-$A_2)$, for which the spin- spin-exchange interaction is large: $2J = 79 \pm 1$ mT. Subsequent laser excitation of $A_1^{-\bullet}$ during the lifetime of $^1(D^{+\bullet}$-$A_1^{-\bullet}$-$A_2)$ rapidly produces $^1(D^{+\bullet}$-A_1-$A_2^{-\bullet})$, which abruptly decreases $2J$ 3600-fold. Subsequent coherent spin evolution mixes $^1(D^{+\bullet}$-A_1-$A_2^{-\bullet})$ with $^3(D^{+\bullet}$-A_1-$A_2^{-\bullet})$ resulting in mixed states which display transient spin-polarized EPR transitions characteristic of a spin-correlated radical ion pair. The influence of deuterated solvents and temperature on the coherence lifetimes will be discussed. These photo-driven *J*-jump experiments show that it is possible to use fast laser pulses to transfer electron spin coherence between organic radical ion pairs and observe the results using an essentially background-free time-resolved EPR experiment.

Sequential Spin-Correlated Radical Pairs in Axial Donor-Porphyrin-Acceptor Triads

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Light–induced sequential electron transfer generates a series of spin-correlated radical pairs, which can be studied using transient EPR spectroscopy. The spin polarization patterns of the radical pairs and their time development contain information about the electron transfer kinetics and its spin selectivity. This information can be extremely useful in guiding the design of donor–acceptor complexes for use in solar energy conversion. Here, we report on a series of axially bound triads based on Al(III) porphyrin (AlPor) as shown in Fig. 1. In the triads, TTF-$(Ph)_m$-py→AlPor-$(Ph)_n$-A, the electron acceptor, A is attached covalently to the Al(III) centre and is either naphthalene diimide or C_{60}, while the secondary donor tetrathiafulvalene (TTF) coordinates to Al(III) via an appended pyridine (py) on the opposite face of the porphyrin ring. Excitation of the porphyrin at room temperature in solution, leads to two-step charge separation between the donor and acceptor. We have studied the spin-polarized transient EPR spectra of the radical pair as a function of the length of the bridging groups, nature of the acceptor and solvent used. The observed spectra can be described well using an analytical model developed by Kandrashkin et al.[1] and they show evidence of singlet-triplet mixing in the initial radical pair. From the evolution of the electron spin polarization, the singlet back reaction lifetime can be estimated and a lower limit for the triplet recombination lifetime is also obtained.

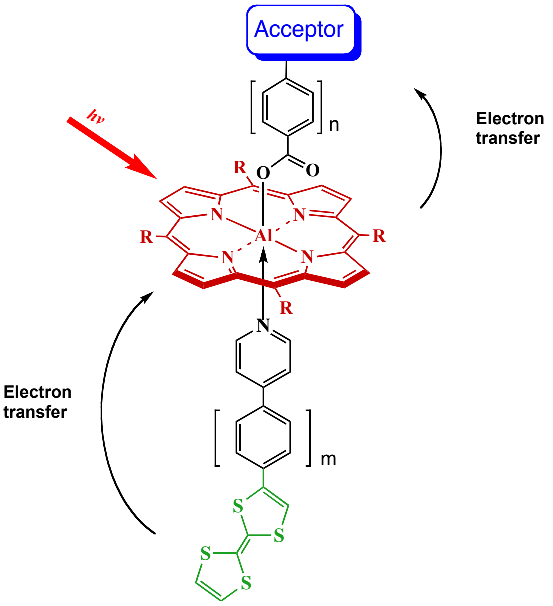

Fig. 1 Structure of the Al–porphyrin triad

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Time-resolved and field dependent CIDNP study of radical reactions of peptides with sulfur containing amino acids

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Sulfide radical cations are often implicated as likely intermediates in assorted biological electron transfer reactions. They can be stabilized through intramolecular complexations with neighboring groups providing electron lone pairs and formation of sulfur-oxygen, sulfur-nitrogen, and sulfur-sulfur two-center three electron bond. The purpose of this investigation was to follow the neighboring group effects resulting from the interactions between the sulfur radical cationic site from methione or cysteine residue and nearby lone-pair electrons on heteroatoms in the peptide bonds. Combined application of time-resolved and field dependent photo-CIDNP was exploited to glean information about short-lived radicals of sulfur containing amino acids that are too elusive to be observable by standard techniques such as EPR. First, a strict linear correlation between the hyperfine coupling constants and the NMR signal amplitude for geminate reaction products was utilized to identify the spin density distribution in radicals. Pulsed CIDNP with microsecond time resolution provides information about rate constants and mechanism of the reactions. Second, by variation of CIDNP amplitude as a function of magnetic field a distinct dependence of nuclear polarization on the external magnetic field was revealed, thus providing precise information about g-factors of two-center-three electron bonds between sulfur and different heteroatoms. Comparative study of sulfur containing amino acids methionine and methyl cysteine and of peptides containing these amino acids with various co-residues was performed to reveal the neighboring-group effects with formation of two-center three electron bond between the initially formed sulfur radical cations and the heteroatoms associated with the peptide bonds or with neighboring residue. We identified, characterized, and quantified different complexed sulfide radicals from various enantiomeric forms of cyclic peptides.

Acknowledgement. This work was supported by the program of the Russian Government P220 (grant No.11.G34.31.0045), RFBR (projects No. 11-03-00296, 13-03-00437-a), Division of Chemistry and Material Science RAS (project 5.1.1), the program of the President of Russia to support the leading scientific schools (No. NSch-7643.2010.3).

Interpretation of the CIDNP field dependence: the importance of polarization transfer in diamagnetic reactions products

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CIDNP is a method, which can indirectly detect free radicals by studying NMR signals of their diamagnetic reaction products. It is sensitive to radicals with lifetimes on the nanosecond timescale; the technique is applicable at physiological conditions and can be used for investigating pathways and kinetics of radical reactions and determining magnetic parameters of elusive free radicals. By studying the CIDNP intensity and its magnetic field dependence one can determine magnetic interactions in radical pairs (RPs) such as hyperfine couplings (HFC), electronic *g*-factors and exchange interactions. A strategy to extract these parameters is measuring CIDNP as a function of the external magnetic field and modeling it using suitable theoretical approaches. For RPs in solutions of normal viscosity where the electronic exchange interaction is negligible usually two regions in the CIDNP field dependencies are expected where characteristic features are observed. At low field, comparable to the effective HFC, a_{eff}, in the RP, features are conditioned by a HFC driven mechanism of triplet-singlet conversion. In a second (high-field) region the CIDNP amplitude is given by $a_{eff}/\Delta g$ and has extrema resulting from the interplay of the HFC- and Δg-mechanisms of spin conversion. For organic RPs the two field regions are well separated from each other because a_{eff} is a few 10 mT or lower, whereas $a_{eff}/\Delta g$ is a few T. From around 10mT to 1T net polarization is expected to be zero. This behavior has led to a strategy of determining HFC and Δg values of RPs. First, HFC constants are obtained from the low-field part; with these values known Δg is then determined from the behavior at high-field. However, there are observations that are not compatible with this approach: at low field often all nuclei acquire comparable CIDNP irrespective of their HFC; in intermediate field rang pronounced features are found not explainable by any of the mechanisms of triplet-singlet conversion in RPs. These findings indicate that alternative mechanisms are operative for CIDNP: it is affected not only by its formation process in the RP reaction but also by spin evolution in the reaction products, in particular by polarization transfer resulting from strong coupling of spins by scalar interaction. Details of this process will be discussed.

Bipolar organic spin valves; Magneto-spectroscopy; Magnetic field effects in fullerenes

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In this talk important advances in the field of Organic Spintronics and magnetic-field response of organic films and optoelectronic devices that we have studied during the past year will be surveyed and discussed.

(i) Organic Spintronics: We have recently demonstrated spin organic light-emitting diode (spin-OLED) using two FM injecting electrodes, where the electroluminescence depended on the mutual orientation of the electrode magnetization directions [1]. This development has opened up research studies into organic spin-valves (OSV) in the space-charge limited current regime.

(ii) Magnetic-field effect spectroscopy: It has been demonstrated that the photo-induced absorption spectrum in organic films (where current is not involved) also shows pronounced magnetic field effect lending support for the polaron-pair model of organic magneto-resistance (OMAR) [2].

(iii) Magnetic field effect and spintronics in fullerenes: It has been shown that even in the absence of the hyperfine interaction, fullerene based devices show limited spin diffusion length and sizable OMAR effect, attesting that the organic MFE has a much broader scope than believed before [3].

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Can open shell chemistry contribute to electron spin science/spin technology of quantum computing and quantum information processing?

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The field of quantum computing/quantum information processing (QC/QIP) has been emerging a new phase since 2012 Nobel Prize for Physics was awarded to two pioneers who first manipulate, independently, a single atom/ion or photon with its quantum nature maintained. These techniques are essential to implement QC/QIP technology. In recent development of QC/QIP, all the relevant physical qubit (quantum bits) systems are facing problems of the scalability of qubits in addition to decoherence intrinsic to their quantum nature. Among many candidates for physically realized qubits, molecular spin qubits are the latest arrival [1], but have their own right [2, 3]. We introduce the latest achievements based on molecular spin qubits in ensemble and discuss their advantages and disadvantages in terms of spin technology [4]. Attempts to apply molecular spins to the implementation of QC/QIP have been underlain by enormous efforts by organic chemist to synthesise stable molecular spins which fulfil the requirements of qubits for QC gate operations. In terms of the gate operations, we utilise weakly exchange-coupled multi-partite electron spin systems because of the limitations of current pulse microwave technology. 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.

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Sensitivity enhancement in biomolecular NMR by laser-driven approaches

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Despite its unmatched resolving power, NMR is an intrinsically insensitive technique. This limitation often precludes the application of magnetic resonance to a variety of biomolecular systems where concentration is either intrinsically low or needs to be kept low to avoid aggregation. This lecture will describe how the unprecedented large signal-to-noise enhancements arising from photo-chemically induced dynamic nuclear polarization (photo-CIDNP) in solution can be exploited to improve NMR sensitivity in the context of heteronuclear correlation spectroscopy. Resonances of both side-chain and backbone CH pairs can be enhanced in the context of free amino acids, polypeptides and proteins. Both theory and applications to the structural biology of protein folding will be described. Prolonged high-power laser pulsing during photo-CIDNP may damage the molecules of interest and reduce the effective concentration of the light-absorbing photosensitizer. This lecture will also introduce a novel tri- enzyme system developed in our lab to significantly overcome this challenge.

Initial Molecular Photocurrent: Nanostructure and Motion of Weakly Bound Charge-Separated State in Organic Photovoltaic Interface

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Organic bulkheterojunction (BHJ) blend films composed of the conjugated polymers as the electron donors (D) and [6,6]-C_{61}-butyric acid methyl ester (PCBM) as the electron acceptor (A) have been widely known to be useful for the highly efficient photovoltaic device as the organic thin film solar cells. Recent studies have demonstrated that the photoinduced, contact charge-transfer (CT) states are initially generated at the D/A domain-interfaces and play significant roles on the photocurrent generations. One of the most puzzling subjects has been that the photocarriers are escaped from the CT binding by the Coulomb attraction which energy is several hundreds of meV, leading to the photocurrent. When the regioregular poly(3-hexylthiophene-2,5-diyl) (RR-P3HT) in which each monomer unit possesses head-to-tail hexyl configuration is utilized, the polymer chains tend to stack into the planar lamellae structure. This structure enhances the interchain hole-mobility to contribute to the higher incident photon to current efficiency (IPCE) in the bulkheterojunction solar cells than in the case that the regiorandom P3HT (RRa-P3HT) is adopted, in which the head-to-tail and the head-to-head hexyl configurations are coexisting. Despite the importance to understand how the interfaces play roles for the carrier dissociations, no study has experimentally characterized the conformational structure, the electronic interactions and the motions of the long-range charge-separated (CS) states that can conduct the photocurrents in the organic photovoltaic (OPV) systems. To elucidate the molecular mechanism of the efficient photocarrier generation by the photoactive bulkheterojunction layers of the OPV devices, we have employed the time-resolved electron paramagnetic resonance method on the solid blends composed of PCBM and P3HT with different regioregularities. The photoinduced CS states have been detected at the boundary regions between the P3HT and PCBM domains to characterize molecular geometries, electronic couplings, and molecular motions for the photo-carrier dissociations.[1]

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Charge Separation in Organic Solar Cells probed by Transient EPR

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Photoinduced charge transfer and subsequent charge separation are the key processes in organic solar cells. Prior to exciton separation into free charge carriers, bound polaron pairs (also referred to as charge transfer states) form at the donor/acceptor interface. While the existence of charge transfer states was confirmed by optical spectroscopy and electrical measurements, their exact role in the process of free charge carrier generation is subject to ongoing discussions. Thus, experimental techniques capable of detecting charge transfer states and providing direct access to their dynamics are highly demanded.

Here we report transient electron paramagnetic resonance (trEPR) measurements performed on a polymer:fullerene blend comprising polythiophene (P3HT) as electron donor and a fullerene-based electron acceptor (PCBM). We show that the trEPR spectrum immediately following photoexcitation reveals signatures of spin-correlated polaron pairs and thus decisively differs from the spectrum of separated polarons commonly observed in light-induced cwEPR. The pair partners (positive polarons in P3HT and negative polarons in PCBM) can be identified by their characteristic *g* values. The fact that population of the polaron pair states strongly deviates from Boltzmann equilibrium unambiguously shows that both constituents of each pair are geminate, i.e., originate from one exciton [1]. We discuss the role of coupled polaron pairs in mediating the conversion from excitons into separated charge carriers and analyse the influence of the temperature on the charge-separation dynamics. Further, we address the differences and similarities between charge transfer states in polymer:fullerene blends and spin-correlated radical pairs in biological systems.

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Light-induced Generation and Coherent Manipulation of Entangled Quantum States in Molecular Crystals

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Huge nuclear spin polarization has been observed in organic triplet states at level anti-crossing (LAC) conditions [1-3]. So far, however, the quantum mechanical mechanism responsible for the nuclear hyperpolarization was not identified. Here, we explore this mechanism using pulsed low-field NMR in combination with pulsed laser excitation. The model system for our studies is triplet pentacene embedded in a host single crystal. On the basis of an analytical theory, the results can be summarized as follows: First, a laser pulse generates the triplet state and initiates the formation of multipartite entanglement between the electron spin and 14 hyperfine coupled proton spins. This gives rise to huge oscillatory electron and nuclear spin polarization. Then, by the action of a resonant high-power microwave pulse, the electron spin is disentangled from the nuclear spins. As a result, the longitudinal nuclear magnetization evolves separately under the nuclear spin Hamiltonian. Due to robust entanglement among the 14 proton spins, one observes quantum oscillations [4] at the nuclear Larmor frequency.

Thus, at triplet LAC conditions, a multitude of entangled nuclear spin states is created simply by light excitation. In case of perfect crystal alignment, we expect ultra-long spin coherence times of several hundreds of seconds. Using pulsed low-field NMR techniques, the entangled spin states can be detected and coherently manipulated in the time domain. Because of the huge polarization of the nuclear spins, these quantum systems are capable of room temperature operation. This makes them promising candidates for various applications in quantum information science.

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Exploring PHIP in Heterogeneous Catalytic Hydrogenations

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Parahydrogen-induced polarization (PHIP) of nuclear spins is an established hyperpolaization tool for various NMR and MRI studies. In the conventional implementation of PHIP, a dissolved transition metal complex is present in the reaction solution along with the reactants and the hyperpolarized products. This is a severe drawback for practical applications such as advanced in vivo MRI/MRS, as the presence of the metal in the administered fluid is not acceptable. This can also complicate the fundamental studies of the PHIP phenomenon.

The scope of PHIP methodology and applications can be significantly broadened by extending it to heterogeneously (HET) catalyzed hydrogenation reactions [1]. HET-PHIP can be potentially used for the hypersensitive in situ NMR studies of heterogeneous catalytic reactions and for the production of gases and catalyst-free hyperpolarized liquids for MRI. We show that immobilized metal complexes of different nature are able to produce strong PHIP effects. We have also successfully observed PHIP in liquid-solid and in gas-solid heterogeneous hydrogenations catalyzed by supported metals, with the PHIP effects being sensitive to the metal nanoparticle size, the nature of the metal and support, and the type of reactants used. These results open new domains in the PHIP research. In addition, they show that at least some of the previously published results on homogeneous PHIP may have been misinterpreted, as the assumed homogeneous nature of the reaction was not verified.

Applications of HET-PHIP for the imaging of gas flow in microfluidic chips and of the progress of a catalytic reaction in a microreactor have been successfully demonstrated, but the attempts to further improve the PHIP technique are in progress. The most recent developments include the demonstration of HET-PHIP with the new classes of heterogeneous catalysts, the new ways of producing catalyst-free hyperpolarized fluids, and the novel approaches for the use of parahydrogen to produce hyperpolarization of nuclear spins.

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Some new magnetic field effects in solution chemistry

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The influence of a magnetic field on processes occurring in solution in an electrochemical cell is often unexpected, but most of the observed effects are traceable to convection. The Lorentz force $\boldsymbol{F}_L = \boldsymbol{j}\times\boldsymbol{B}$ exerted on an electric current density $\boldsymbol{j}$ flowing in a field $\boldsymbol{B}$ drives magnetohydrodynamic convection (MHD). The Kelvin force $\boldsymbol{F}K = (1/\mu0)c\chi\nabla B^2$ acting on paramagnetic species in solution with concentration c and susceptibility χ can also induce convection when orthogonal concentration and magnetic field gradients are present. The resulting perturbation of the diffusion layer modifies mass transport, with striking effects on electrodeposition. However, the electrode/electrolyte interface is the seat of electrochemical redox reactions, which are controlled by the structure of ions and solvent molecules in an interfacial double layer 0.5-10 nm thick. It is here that we find a new effect of magnetic field. A 0.5 T field can modify the capacitance and charge transfer resistance of the double layer by up to 50%. The effects observed in nitrobenzene, a model electrochemical system, imply a shift of the outer Helmholtz plane by a few tenths of a nanometer, which can be explained by Maxwell stress acting on the paramagnetic $NB^{\bullet-}$ radicals in solution near the electrode. There is therefore a prospect of using magnetic fields to explore the internal *terra incognita* lying a nanometer or so from the electrode surface, and perhaps control critical interface phenomena involving nucleation of electrodeposits or magneto-electrostatic gating.

In a second part, we revisit claims long regarded as fantastic, that a magnetic field could modify the precipitation of calcium carbonate from aqueous solution long after the water has left the region where the water was exposed to the magnetic field. We have no new experimental evidence to offer, but we describe how such an effect could be rescued from the realms of fantasy, based on the existence of nanoscale prenucleation clusters of hydrated calcium carbonate which are now thought to exist in equilibrium. While flowing through a nonuniform magnetic field, precession of proton spins leads to modification of the nuclear singlet/triplet ratio, which results in long-lived chemical modification of the surface of the nanoscale clusters. A condition $(L/v)f_p a\nabla B \approx 1$ is derived, where L is the channel length through which water flows with velocity v which corresponds to the design of the magnetic water treatment devices. Here a is an interatomic distance and f_p is the proton Larmor precession frequency.

Organic Magneto-Resistance in the Presence of Strong Magnetic-field Gradients

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Organic spintronics is concerned with the study of spin-injection and magnetic-field dependent transport phenomena in organic semiconductors. In addition to widely known spin-valve effects, there exists a large room-temperature magnetoresistive effect in organic devices made entirely from non-magnetic materials, the so-called organic magnetoresistive (OMAR) effect, which has no analogue in inorganic spintronics. OMAR is known to be caused by the variation from hopping site to hopping site of the nuclear hyperfine field, and this can dramatically affect the electronic hopping transport in organics. We demonstrate a third, new method of controlling the electrical conductivity and electroluminescence of an organic film at room temperature, using the spatially-varying magnetic fringe fields of a magnetically-unsaturated ferromagnet [1]. Surprisingly these inhomogeneous fringe fields vary over length scales roughly two orders of magnitude larger than the hopping length in the organic materials, and the theoretical explanation of the effect is more challenging than hyperfine-related models of magnetotransport. We explain the experimental magnetoresistance traces using a model based on differential electron spin precession in magnetic field gradients [2]. Our devices, which do not rely on spin injection, tunneling anisotropic magnetoresistance or spin-valve behavior, may provide a simple approach to integrating magnetic metals and organics for hybrid spintronic devices. These devices may find application as high-voltage readouts of the magnetic state of low-impedance ferromagnetic films.

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Entanglement-based magnetometry and enhancing sensitivity of chemical magnetometers with optical control

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Magnetic field effects in the radical pair mechanism can be used for chemical magnetometry and constitute the basis of a primary hypothesis for animal magnetoreception. For systems of radical pairs in solution, we present two strategies for magnetometry.

First, we discuss how signatures of entanglement in the spin degree of freedom of radical pairs can be used for magnetometry. For the experimentally well-studied model system of pyrene and N,N-dimethylaniline (DMA), we present an observable, i.e., an entanglement witness, that detects entanglement and we discuss the impact of experimental imperfections in conceivable measurement procedures.

Second, we propose an experimental approach based on molecular photoswitches to achieve additional control of radical pair reactions at the level of the recombination dynamics [1]. This approach allows for short-time resolution of the spin dynamics and it enables experiments to test some of the standard assumptions of the radical pair model. As an application, we present a scheme using pulsed lasers that improves the sensitivity of a model system for a chemical magnetometer by two orders of magnitude.

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Realization of huge magnetic field effects in organic devices

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Substantial magnetic field (B) effects (MFEs) of up to 30% in the current and luminescence of organic light-emitting diodes have recently been found by researchers active in the field of Organic Spintronics. Evidence is growing that these MFEs have a similar origin as the MFEs in chemical reactions as studied in Spin Chemistry. The „polaron-pair“ mechanism used in Organic Spintronics, describing the B-dependent formation of a singlet or triplet exciton from an electron and hole polaron, is in spirit identical to the „radical-pair“ mechanism used in Spin Chemistry. The field of Organic Spintronics can profit from the richness of ideas developed in Spin Chemistry, in particular those related to donor-acceptor systems.

We argue that it should be possible to manufacture organic materials and devices based on donor-acceptor systems that show essentially on-off switching by a magnetic field. The key idea is to combine spin and charge blocking in a one-dimensional (1D) system. We have calculated that a system consisting of a 1D alternation of donor and acceptor units could show a magnetoconductance of –98.5% under optimal conditions [1]. We think that it should be possible to synthesize donor-acceptor polymers that satisfy these conditions.

Very recently, magnetoconductances of close to –100% were found in 1D molecular wires consisting of π-conjugated molecules inserted into the channels of zeolite crystals [2]. We think that the mechanism behind these huge magnetoconductances is very similar: spin blocking of electrons takes place by molecules that already hold an electron and can only accept another electron with an opposite spin. Positively charged potassium ions in the channels could possibly stabilize the doubly negatively charged molecules.

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TREPR spectra of TEMPO radical covalently-linked to naphthalene: Quenching of excited singlet and triplet states, and appearance of splitting

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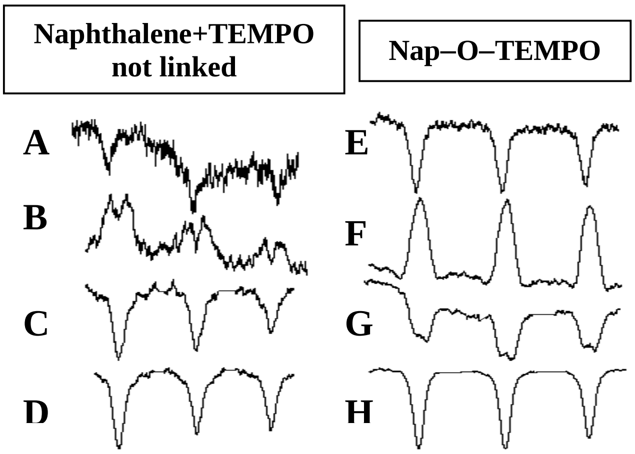
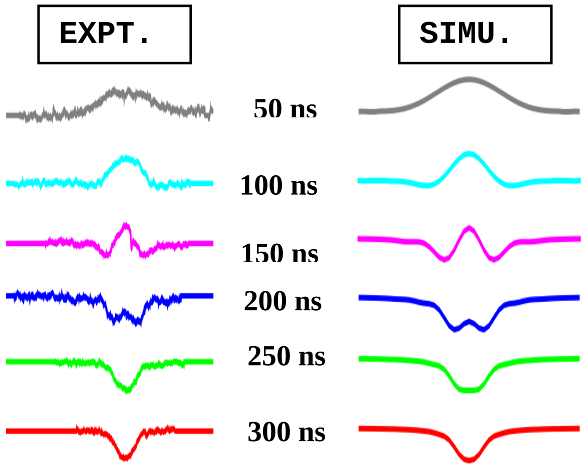
We have synthesized molecules of the type Nap–Sp–TEMPO where the naphthalene chromophore (Nap) is covalently linked to the TEMPO free radical through a variable length spacer group (Sp). When naphthalene was excited and quenched by the radical, the TREPR spectra of TEMPO showed interesting time evolution, greatly varying with the size of the spacer group (Figure at right). Around –40 °C, the directly-linked molecule Nap–O–TEMPO showed fast evolution from absorptive to emissive spin polarisation with peculiar splittings appearing in each hyperfine line in intermediate times. Somewhat similar, but not exactly the same, behaviour was seen when naphthalene and TEMPO were not linked, but present as separate molecules. This effect was not seen with longer spacer groups.



Temp.:A, E: 22°C; **B-D, F-H**: ca. –40°C. **Time: A, E**: 0.5 μs; **B**: 0.1 μs; **C**: 0.3 μs; **D**: 0.5 μs; **F**: 0.1 μs; **G**: 0.2μs; H:0.5 μs.

We have modelled the dynamics of the quenching process and the generation of RTPM electron spin polarisation as sequential quenching of the singlet and triplet states of the naphthalene moiety. By incorporating this into the time-dependent Bloch equations, we simulated the evolution of the spectra using the measured values of most kinetic parameters. The figure at left shows the experimental and simulated TREPR of the central hyperfine line of Nap–O–TEMPO molecule at various times after the laser pulse. Most observed features could be satisfactorily reproduced in the simulations.



Magnetic Field Effect to identify distance-dependent phenomenon: Photoinduced electron transfer between DNA and metal complexes

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Application of low magnetic field (MF) of the order of 0.01-0.02 tesla helps enormously in the elucidation of the reaction pathways of photoinduced reactions that involve either geminate radical ion pairs or radical pairs as transient intermediates produced through photoinduced electron transfer and hydrogen abstraction or bond cleavage respectively. The radicals when separated by a certain distance by diffusion where exchange interaction becomes negligible might undergo maximum intersystem crossing by spin flipping in the presence of an internal MF i.e. hyperfine interaction (HFI) present in the system. Application of an external MF which can overcome HFI reduces the intersystem crossing leading to an increase in recombination product or free ion formation, which is a ‘signature of the initial spin state of the radical ion pairs’, either singlet or triplet respectively. Moreover, MF effect is able to signify the ‘optimum separation distance’ where maximum spin flipping and formation of free ions or recombination products occur [1]. Biological macromolecule itself provides a confined and restricted environment sustaining the geminate characteristics of the radical pairs or ion pairs even at the optimum interradical separation distance. We studied the mechanism of electron transfer phenomenon occurring between calf thymus DNA and 1,10-phenanthroline (phen) - copper (II) complex and its amino acid substituted homologues, on photo-excitation using laser flash photolysis and MF effect. The occurrence of partial intercalation of the complexes within DNA helps in maintaining that proper inter-radical distance between the radical ion pairs generated through photoinduced electron transfer [2]. Recently we have synthesized different copper (II) Schiff base complexes with different heterocyclic nitrogen containing ligands with different structural substitutions which undergo photoinduced electron transfer with DNA in triplet state. The unsubstituted complex system shows greater $B_{1/2}$ value, the field at which half the saturation of the effect reaches and a measure of hyperfine interaction present in the system, than the substituted one in presence of DNA. The result indicates the role of multistep hopping phenomena in DNA caused by the unsubstituted complex which can approach much closer to DNA than the substituted one which remains far-off due to steric hindrance.

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Poster Abstracts

NMR and Photo-CIDNP Studies of the Photocatalytic Coupling of Tertiary Amines with Nucleophiles

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The fast developing field of photocatalysis and thus the investigation of their reaction mechanisms became more important in recent years. However, most of the reaction mechanisms are still not fully known. Therefore the aim of our work is the investigation of the key steps of the photocatalytic coupling of tertiary amines with nucleophiles, using ruthenium(II) polypyridine complexes as catalysts [1,2]. Photo-CIDNP spectroscopy is a powerful tool for the investigation of radical reaction mechanisms [3,4] and is therefore applied for our studies on the upper reaction system. For our measurements we use a setup consisting of a blue light-emitting diode and an optical fiber, which is guiding the light directly into the sample. This setup enables time-resolved CIDNP spectroscopy on a millisecond timescale. Further, this setup provides an easy method for the detection of diamagnetic intermediates and their kinetics. Former studies of ruthenium(II) polypyridyl complexes, performed by Perrier *et al*. [5], show the ability of ruthenium(II) complexes for Photo-CIDNP spectroscopy.

First results show Photo-CIDNP signals in low intensities for the ruthenium(II) polypyridine complex as well as for the expected isoquinoline species, which is formed by electron transfer from the excited catalyst to the tetrahydroisoquinoline. Further, tetrahydroisoquinolinium, an isoquinoline dimer and hydrogen peroxide were successfully detected by means of NMR. These diamagnetic intermediates and side products were investigated by kinetic studies.

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Experiment and theoretical investigation of CIDNP field dependence in linked system

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Intramolecular electron transfer is actual, due to the presence of this phenomenon in important chemical and biochemical processes. Linked systems are the molecules, where donor and acceptor groups divided by molecular bridges, and widely used as a model for the studying of electron transfer in photosynthetic systems, enzymes and other biologically relevant systems.

With the help of spin chemistry it has established, that degradation of the exited state of the donor-acceptor dyad [S, R]-N-methyl-2-2-pyrrolidinmetyl[S]-(6-methoxy-2-naphthyl) propionate the reversible electron transfer is carried out in the system. It was shown that exiplex is also forming during degradation of exited state of the dyad. Dynamic equilibrium between exiplex and ion biradical leads to unusual dependence of CIDNP on solvent polarity.

Now for the further inquiry of short-lived intermediates of the reaction we have registered the CIDNP field dependence and theoretically described it using earlier investigated approach modified for taking into account of 2 magnetic nuclears. In high polarity the dependence has a form usual for the reaction with biradical formation – curve with one extremum. It allows determining the exchange interaction J. The dependence in low polarity shows a small shift of the extremum indicating the changing in biradical conformation and of value of J. Also the dependence in low solvent polarity demonstrates alteration of the CIDNP sign. This effect can be modeled theoretically with essential increasing of the biradical live time.

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Spin selective recombination as the source of hyperfine excitation of hydrogen atoms

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Hydrogen is the active participant of physics and chemical processes in space as well as on earth. Recombination of hydrogen atoms is the electron spin selective process producing diamagnetic H_2 molecules. The spin selectivity of recombination is determined by Pauli's principle and the angular momentum conservation law. If the hydrogen atoms are initially in the ground singlet state $\left|S_{\blacklozenge}\right\rangle = 2^{-1/2}\left|\alpha_e\beta_{\blacklozenge} - \beta_e\alpha_{\blacklozenge}\right\rangle$

(α_e ,β_e - electron spin states, α_n ,β_n- nuclear spin states) then H_2 has been proved to be created in the *para* -H_2 state only. If atomic pairs (H+H) are in triplet electron states, they can't recombine and produce separated H atoms. These H atoms are shown to be in the statistical mixture of the ground and exited hyperfine states and can be described by the spin density matrix only $\rho_H = \frac{1}{16}|T_+\rangle\langle T_+| + \frac{1}{16}|T_-\rangle\langle T_-| + \frac{1}{16}|T_0\rangle\langle T_0| + \frac{9}{16}|S\rangle\langle S|$ here $\rho_H = Tr_2\rho$ (Tr_2 - the trace over variables of the second atom). The probability of excitation is determined by the probabilities P_T of triplet hyperfine states; all P_T = 1/16 if the magnetic field is absent. The other hydrogen atoms leave the contact state being in the ground singlet state.

The magnetic field makes the hydrogen ground state a mixture of the singlet and the triplet states. The admixture of the triplet state decreases the probabilities of recombination and excitation $W_s = \frac{1}{4}a^2/\left(a^2 + (\omega_e + \omega_n)^2\right)$ $W^* = \frac{1}{16}a^2/\left(a^2 + (\omega_e + \omega_n)^2\right)$ here *a* – *HFI* constant, $\omega_{e,n}$ – electron and nuclear Zeeman frequencies. Thus, the magnetic field decreases the recombination probability. Strong magnetic fields are able to switch the recombination off. Simultaneously magnetic field decreases the excitation probability for hydrogen atoms that were not able to recombine in contact pairs (H + H).

Conclusions: 1. The "unsuccessful" attempts of spin selective recombination can be the source of excited hydrogen atoms. 2. Populations of excited hyperfine states are determined by coefficients of the spin density matrix. 3. Strong magnetic fields decrease the recombination probability and populations of hydrogen excited states simultaneously. 4. Recombinational excitation can be the origin of excited hyperfine states in hydrogen atoms in the universe, which are the source of the space radio frequency emission (ν = 1428,5714 MHz).

Towards a comprehensive computational model of flavin spin chemistry

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In the past years a wide variety of flavin-containing proteins serving as non-visual photoreceptors has been identified and extensively studied. The response of the flavoproteins to light is mediated though formation of spin-correlated radical pairs signifying a novel mechanism implicated in biological light sensing. Sensitivity of these radical pairs to the magnetic field, demonstrated in cryptochromes and DNA photolyases, prompted a hypothesis that these flavoproteins can be employed in sensing the Earth magnetic field. Along with sophisticated experimental studies of the radical pairs, computational characterization is required in order to understand principles governing the underlying electron transfer reactions. We have been developing an approach, based on *ab initio* and DFT quantum-chemical calculations [1-5], which allows us to determine reaction coordinates of flavin radical pairs in singlet and triplet states and also to characterize the singlet-triplet interactions via spin-orbit coupling. Using this approach, mechanisms of the triplet formation in various flavin-containing photosensing proteins are described and compared. Our calculations provide a basis for understanding the competition of formation, recombination and stabilization of radical pairs, which constitutes the key element of flavin-based magnetosensitivity.

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Analysis of nutation patterns in Fourier-Transform NMR of non-thermally polarized multispin systems

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The complex spin order of hyperpolarized multispin systems giving rise to anomalous NMR spectral patterns that vary with the RF excitation angle is analyzed by decomposing its nutation behavior in a superposition of Fourier harmonics. The product operator formalism is applied to calculating the spectral contributions of the various mutual alignments of scalar coupled spins. Two cases are treated, namely systems exhibiting only differences in population of their spin states and systems showing in addition zero-quantum coherences between states, a situation often seen at hyperpolarization. After deriving the general solution a number of representative examples are discussed in detail. The present treatment allowed us to understand both the flip angle dependence and the NMR spectral patterns of the spin systems carrying multispin order. The theoretical treatment is applied to analyze spin order in a hyperpolarized two-spin system prepared in the singlet state.

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The Excited Triplet State and Spin Polarization Transfer studied in the system of Ir(C$_8$ppy)$_3$ and tetracene

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Iridium complex, Ir(ppy)$_3$, is widely used as a high efficient electro-luminescent material in organic light emitting diode. It is known that a center heavy atom with d-orbit induces the fast intersystem crossing, and phosphorescence is emitted efficiently by fast radiative rate. Moreover, the triplet substates are separated enormously ($D = 160$ cm^{-1}, and $E = 9.5$ cm^{-1}) as reported presiouly[1]. For further investigation of its propety, we used Ir(C$_8$ppy)$_3$, where each ligand was modified by an octyl group to increase its solubility in toluene. Tetracene is mixed with the solution and a time-resolved electron paramagnetic resonance (tr-EPR) method was used in combination with optical measurements. Here, tetracene is employed as an electron and/or energy acceptor. The tr-EPR spectrum is shown in Figure 1. This spectrum is composed of two different excited triplet states. One is the excited triplet state of tetracene and another is that of an unidentified species. At this stage we propose that the latter species is due to the electron-donor-acceptor (EDA) complex that is formed through electron transfer process from Ir(C$_8$ppy)$_3$ to tetracene by way of the excited triplet state. On the other hand, enhanced fluorescence from Ir(C$_8$ppy)$_3$ is observed in this mixed system. Analysis of the spin polarization and its flourescece enhancement will be presented to presume the property and structure of the EDA complex with brief theoretical explanation.

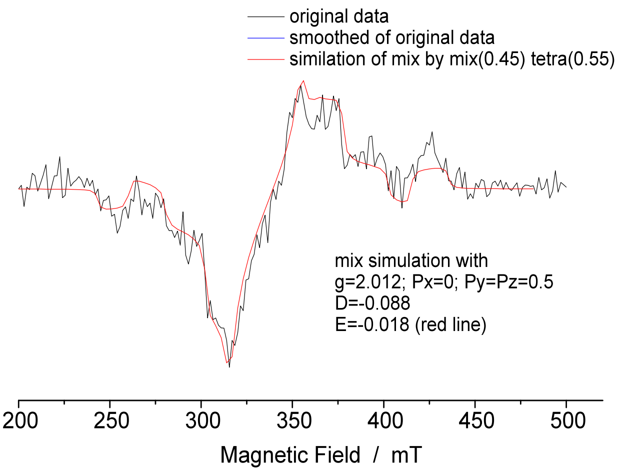

Figure 1 Tr-EPR spectra of 0.10 mM Ir(C$_8$ppy)$_3$ + 1.0 mM Tetracene system in toluene solution observed at 0.8 µs after laser irradiation at 77 K. The red curve is simulation data as a combination with the excited triplet state of the EDA complex and that of tetracene.

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Exciplex kinetics probed by time-resolved magnetic field effect

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The experimental investigation of magnetic field effects (MFE) in exciplex-forming organic fluorophore-quencher systems, where quenching occurs *via* photo-induced electron transfer, is reported. By using the time-resolved exciplex emission, we are able to extract information about the electron transfer reaction mechanism [1]. The initial radical ion pair can originate from the fluorophore-quencher pair directly *via* distant electron transfer or, indirectly, *via* dissociation of an initially formed exciplex. Which reaction channel prevails, depends strongly on the driving force [2]. Since the exciplex dissociation is a slow process, the ions resulting from the exciplex dissociation will be delayed with respect to those formed by direct electron transfer. As a consequence the MFE generated by the exciplex will also be delayed. In this way the time-resolved MFE allows discriminating both reaction channels. In order to change the driving force of the charge separation, we have varied the fluorophore and the quencher: 9,10 dimethylanthracene (DMAnt), 9-methylanthracene (MAnt), and anthracene (Ant) have been chosen as the fluorophores; N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA), and N,N-dimethyl-*p*-toluidine (DMTO) as the quenchers. The effect of preferential solvation on the exciplex emission has been studied as well using homogeneous binary solvent system (propylacetate/butyronitrile) with increasing in the relative permittivity of the solvent environment [3].

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Magnetic Field Effects on Upconverted Delayed Fluorescence in Solutions Through Sensitized Triplet-Triplet Annihilation

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Photon upconversion based on sensitized triplet-triplet annihilation (TTA) is the technology with the promis in applications such as photovoltaics and imaging. Typically, photon upconversion results in p-type delayed fluorescence of triplet acceptor molecules. While magnetic field effects (MFE) on such delyaed fluorescence through TTA are well known [1], only a few examples of this effect in solution are known. Here we present large MFE, up to 10%, on TTA-sensitized visible emission in solutions at room temperature using near-infrared absorpbing metallopophyrins as sensitizers. This demonstration suggests the possibility of using this type of magnetic modulation of emission in imaging applications.

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Specific Solvation on Radical Ion Pair Studied by MARY Line-Broadening Experiments

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This work aims at providing deeper insight into the solvation mechanism of the transient Radical Ion Pairs (RIP) in mixed solvent systems [1,2]. MARY line-broadening measurements have been undertaken on the 9,10-dimethylanthracene(DMAnt)/ *N,N*-dimethylaniline(DMA) system in a micro-heterogeneous (toluene/dimethylsulfoxide (DMSO)) and a quasi-homogenous (propyl acetate/butyronitrile) solvent system of variable compositions. The experiments yield the self- exchange rate constants, k_{obs}, and the intrinsic half saturation field strength, $B_{1/2}(c\rightarrow0)$, in the limit of zero quencher concentration by means of extrapolation in the slow exchange regime. The spread in the $B_{1/2}(c\rightarrow0)$ values obtained at various compositions is more pronounced in the heterogeneous solvent mixture as compared to the homogenous one. The kobs increase slightly with increasing polarity in both the solvent systems. The behavior, considering the solvent- dynamic parameters in both the systems has been interpreted on the basis of the local dielectric enrichment brought about by the heterogeneous solvent system which in turn can affect the effective RIP life-time through caging and altered recombination dynamics. We propose that local cluster formation by DMSO molecules in the heterogeneous solvents is operative. A local enrichment of these polar clusters with DMA is detected. Additionally isotope substitution on the binary solvents has been used to show that there is no effect of non-bonded solvent molecules on $B_{1/2}$. A simple continuum model of the heterogeneous solvation process is shown to yield good correspondence with the experimental radical ion pair lifetimes [3].

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The effect of the preferential solvation on exciplex emission revealed by time-resolved magnetic field effects

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The dependence of the magnetic field effects (MFE) of the exciplex emission on the bulk dielectric constant, ε, of the medium has been extensively studied (by varying composition of non-polar and polar solvents) [1]. Steady-state measurements have been undertaken in homogeneous and micro-heterogeneous solutions. Here, we investigate the effect of preferential solvation in micro-heterogeneous (toluene/dimethylsulfoxide mixtures) by means of the time-resolved magnetic field effect. To this end, the exciplex emission of the system 9,10-dimethylanthracene (fluorophore)/N,N-dimethylaniline (quencher) is studied using the TCSPC approach in the presence and absence of external magnetic field. In the micro-heterogeneous environment, the MFE of the exciplex emission occurs at a short timescale in comparison to iso-dielectric homogeneous solvents. Furthermore, the local polarity reported by exciplex is enhanced. These observations provide evidence of polar micro-domain and enhanced caging in micro-heterogeneous binary solvents [2]. The results are analysed in terms of a continuum model of the solvation micro-heterogeneous.

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Studies on B1/2 value of pyrene-dimethylaniline radical pair system in single and binary solvents

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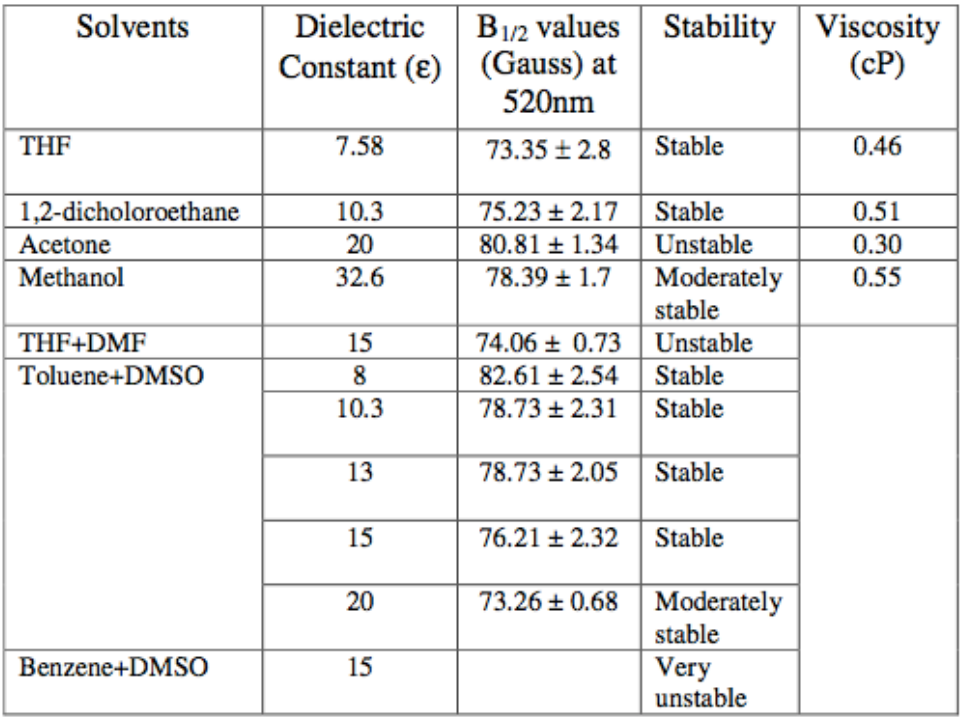
$B_{1/2}$ values of pyrene-dimethylaniline radical pair system in different single and binary solvents have been measured (cf. Table). The data have been explained on the basis of modulation of size of polar micro-domain with change in bulk ε and the variation of $B_{1/2}$ in single solvents has been explained on the basis of diffusivity and specific solvent property like H-bonding. We feel that [1] at the onset of MFE (size of micro-domain, r_d) crosses the value R_{ST} (the distance at which S,T spin states are degenerate) and the hyperfine interaction (HFI) induced inter-system crossing (ISC) starts to play. As the size of the domain increases the effective lifetime of the RIP in the domain of S-T degeneracy increases. Thus we see that as the volume fraction of the polar component is decreased the effective lifetime of the RIP undergoing ISC decreases which leads to broadening of the spin states and the $B_{1/2}$ value increases. An estimate of the domain sizes have been deduced from the uncertainty principle at ε = 8 and ε = 20.



Solvents	Dielectric Constant (ε)	$B_{1/2}$ values (Gauss) at 520nm	Stability	Viscosity (cP)
THF	7.58	73.35 ± 2.8	Stable	0.46
1,2-dicholoroethane	10.3	75.23 ± 2.17	Stable	0.51
Acetone	20	80.81 ± 1.34	Unstable	0.30
Methanol	32.6	78.39 ± 1.7	Moderately stable	0.55
THF+DMF	15	74.06 ± 0.73	Unstable	
Toluene+DMSO	8	82.61 ± 2.54	Stable	
	10.3	78.73 ± 2.31	Stable	
	13	78.73 ± 2.05	Stable	
	15	76.21 ± 2.32	Stable	
	20	73.26 ± 0.68	Moderately stable	
Benzene+DMSO	15		Very unstable	

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Influence of amino-group charge on the oxidation kinetics of aromatic amino acids

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As photosensitized electron and hydrogen transfer between amino acids and endogenous chromophores, such as flavins, porphyrins, benzophenones is important in biological systems, in present work we study photochemical reaction of 3,3′,4,4′-benzophenone tetracarboxylic acid (TCBP) with aromatic amino acids, His, Trp and Tyr. Based on our previous results that reactivity of peptide residues can depend on the presence of charge on the terminal amino group [1], we compared reactivity of free His, Trp and Tyr and theirs acetylated derivatives, N-Ac His, N-Ac Tyr, N-Ac Trp towards TCBP triplets in pH range from 2 to 12 of aqueous solution. Complimentary application of laser flash photolysis and time-resolved CIDNP enabled us to monitor transient triplet intermediates and to get information on transient radical intermediates on the geminate stage of the reaction. As a result, pH dependencies of quenching rate constants of TCBP triplets by His, Tyr, Trp, as well as N-Ac His, N-Ac Tyr, N-Ac Trp was revealed and explained in terms of pK_as of reactants. It was established that the presence of positive charge on the amino group increases by an order of magnitude the efficiency of oxidation reaction of His by TCBP triplets compared to N-Ac His, and by a factor of 4 compared to His with neutral amino group. Tyr and Trp with positive charged amino group are about 3 times more reactive than Tyr and Trp with neutral amino group, as well as than N-Ac Tyr and N-Ac Trp correspondingly.

Support of this project by the Eurasia-Pacific Uninet Program, COST Program, the program of the Russian Government ("Measures to Attract Leading Scientists to Russian Educational Institutions", grant No.11.G34.31.0045), RFBR (project No. 13-03-00437, No. 12-03-33082) is acknowledged.

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Registration of Radical Anions of Al, Ga, In tris-8-oxyquinolinates by Magnetosensitive and Spectrally Resolved Recombination Luminescence

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This work is devoted to two aspects – inorganic short-lived radical ions and radiation spin method called MARY spectroscopy. On one hand we study radical ions of tris-8-oxyquinolinates of Al, Ga and In that have drawn much attention as they are typical electroluminescent and electron transport agents for OLEDs. The control of their luminescent properties and the possible ways of manipulating them is important for raising emission efficiency in these devices. On the other hand, a whole new class of systems will be also opened for spin chemistry studies, including but not limited to MARY spectroscopy. Radical-ionic states of complexes based on central metal ions are very interesting in this respect since the metal ion can have nuclear spin other than 1/2 or 1, to which nuclei in organic radicals are usually limited, and rather high hyperfine couplings to these heavy nuclei. Furthermore, our compounds are very useful for magnetic and spin effect studies as the central ion can be readily changed without changing the ligand environment, and thus a series of similar systems can be generated that can have widely varying magnetic properties.

We synthesized oxyquinolinates of Al, Ga and In and compared their fluorescence under photo- and X-irradiation in benzene solution. The spectra are similar for the two generation methods, and photogenerated luminescence agrees with literature data. The complexes thus produce exited states and luminescence under X-irradiation with relative yields of 1:0.3:0.15 for Al, Ga and In, respectively. Next we obtained MARY spectra for solutions of Al, Ga and In tris-8-oxyquinolinates, which differ from each other, and demonstrated that radical anions of the complexes are detected. The experimental spectra were reproduced with a model taking into account nuclear spins of the central ion of the radical anion. The second moments of the ESR spectra for these complexes were estimated from fitting, and hyperfine coupling constants with the central ion were found to be 0.45, 0.8. and 0.6 mT for Al, Ga and In, respectively.

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Coherent Transfer of Para-Hydrogen Induced Polarization at Variable Magnetic Field

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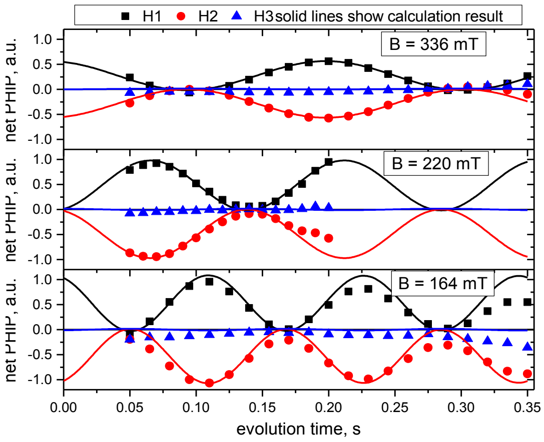
Para-Hydrogen Induced Polarization (PHIP) experiments were performed on phenylacetylene and fluorine derivatives of phenylacetylene at variable magnetic fields. At magnetic fields where spin level anti-crossing occurs (100-400 mT for styrene) we found fast and coherent polarization transfer between coupled spins. Kinetics of the PHIP transfer at magnetic field 164, 220, and 336 mT have been measured using experimental protocol containing two field switches. The system was polarized at 7 T, and then field was rapidly switched down to desire level and after short delay switched back to 7 T. In all cases the kinetic curves have oscillations (see graph insert). Beat frequency depends on the magnetic field. The solid lines on the graph show the numerical calculations for this particular spin system, taking into account the exact profile of the magnetic field variation over time[1]. In addition we studied polarization transfer to ^{19}F nuclei. It is shown that fluorine nuclei can be efficiently and rapidly polarized within less than 50 ms. Thus, the main mechanism of polarization transfer to heteronuclei is a quick passage through the level anti-crossing and not cross-relaxation.



Acknowledgement. This work was supported by Alexander von Humboldt Foundation (ASK and IKL), RFBR (projects No. 11-03-00296, 12-03-31775, 12-03-31042, 13-03-00437), Program of Division of Chemistry and Material Science RAS (project 5.1.1), the program of the President of Russia to support the leading scientific schools (No. NSch-2429.2012.3).

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Relaxation of nuclear-spin hyperpolarization at variable magnetic field

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The aim of this work is theoretical and experimental investigation of the evolution of hyperpolarized nuclear spin systems at variable external magnetic field, most notably, life times of Long Lived Spin States (LLS) populated [1] by means of Chemically Induced Dynamic Nuclei Polarization (CIDNP) technique. The experimental method is based on a combination of high-resolution NMR technique and fast field-cycling. We studied the field dependence of LLS formed by means of CIDNP for amino acids Tyrosine (Tyr) and Histidine (His) and for their selectively labeled derivatives: Tyr-$D_{3,5}$, Tyr-$D_{2,6,\alpha}$, Tyr-$D_{2,3,5,6,\alpha}$, His-$D_{2,\alpha}$, His-$D_{2,4,\alpha}$; several dipeptides were investigated as well.

Field dependences of LLS of the β-protons have been investigated in a field range from 0.1 mT up to 7 T. It was found out that the LLS lifetime increases at low magnetic fields where the strong coupling condition is fulfilled when the number of deuterium-substituted nuclei near the β-protons increases. Maximal LLS lifetimes for the investigated amino acids were found for Tyr-$D_{2,3,5,6,\alpha}$ and His-$D_{2,4,\alpha}$, that are ~26 s and ~55 s, respectively. This is 45 times longer than the T_1-relaxation time for the β-CH_2 in the same compounds at high fields.

We also investigated the LLS behavior theoretically: a description of spin relaxation caused by dipole-dipolar interaction in scalar coupled spin systems has been developed. The results of modeling are in good agreement with the experimental observation of the LLS field dependence. Using the same approach a cross-relaxation mechanism of hyperpolarization transfer was studied. This mechanism is potentially responsible for the hyperpolarization transfer from protons to spin ½ heteronuclei, which takes place in CIDNP and Para-Hydrogen Induced Polarization experiments with variable magnetic field strength.

The research was financially supported by the Russian Fund for Basic Research (projects No. 11-03-00296, 12-03-31042, 12-03-33082), the program of the Russian Government to support the leading scientists (grant No.11.G34.31.0045), the Program of the Division of Chemistry and Material Science RAS (project 5.1.1).

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The influence of high pH in the solid-state photo-CIDNP effect observed in the phototropin LOV1-C57S

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Recently, it has been demonstrated that the solid-state photochemically induced dynamic nuclear polarization (photo-CIDNP) effect can be observed in non-photosynthetic systems [1] and not exclusively in natural photosynthetic organisms. The observations were done in a mutant of a LOV domain of the blue-light photoreceptor phototropin from the green alga *Chlamydomonas reinhardtii* [2]. This member of the family of flavin-containing blue-light photoreceptors includes two LOV domains, each binding noncovalently a flavin mononucleotide (FMN) and a kinase domain. Hence, photo-CIDNP magic-angle spinning (MAS) NMR can be applied to reveal a detailed picture of the functionality of such blue-light photoreceptors.

In a first attempt to study the functionality, photo-CIDNP MAS NMR experiments have been done by changing the pH values. At pH9, the preliminary results show positive signals from the FMN and negatives from a tryptophan residue. The results, compared with those reported [1], indicate that an influence of pH on the photo-CIDNP spectra of this phototropin mutant exists. Currently, more experiments are in progress to confirm these observations.

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An investigation into a novel flavin and *fd* virus chemical compass system using optical spectroscopy methods

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It is speculated that the ability of certain bird species to navigate in the Earth's magnetic field (~50 μT) arises from a photoinduced radical pair reaction in cryptochrome flavoprotein [1]; the recombination kinetics of the system is proposed to be sensitive to the strength and inclination of the magnetic field. This is known as chemical compass behaviour and has yet to be explicitly characterised for cryptochrome in vitro. Flavin mononucleotide (FMN) and *fd wild-type (wt)* virus is proposed as a model chemical compass system. It incorporates the biologically pertinent radical pair precursors of cryptochrome with the potential for alignment in the liquid crystal phase of *fd wt* virus [2]. Using transient absorption (TA) spectroscopy, surface accessible tyrosine residues have been shown to undergo electron transfer with photoexcited FMN to form spin-correlated radical pairs (SCRPs). Although indiscernible by TA spectroscopy, magnetic field effects (MFEs) have been detected through a newly developed Prompt Fluorescence Magnetically Altered Reaction Yield (PF MARY) technique, stimulating future work into the detection of anisotropic field dependence through optimisation and alignment.

The proposed chemical compass system was compared to the FMN and ribonuclease A (RNase A) tyrosine-containing reference system. PF MARY and novel application of Cavity Ring-down Spectroscopy (CRDS) technique are presented, the latter being a sensitive method to elucidate reaction kinetics where conventional TA spectroscopy fails. This is the first protein system in which a low field effect (LFE) was observed under physiological conditions and is significant to the magnetoreception debate as it provides a proof-of-principle for low-field sensitivity relevant to biology.

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Magnetically sensitive light-induced reactions in Drosophila Melanogaster are consistent with its proposed role as a magneto receptor

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Recent papers have shown that Drosophila Melanogaster (Dm), the common fruit fly, changes it behaviour upon the application of an applied external magnetic field. In this poster we describe experiments with DmCry proteins expressed from Ecoli that display magnetically sensitive reactions, and propose how the magnetic sensitivity of these reactions could be a key component of a biological magneto-sensing mechanism in Drosophila Melanogaster. In this proposition transient radical pairs formed by photo-induced electron transfer reactions in cryptochrome proteins have coherent spin dynamics that are influenced by applied magnetic fields and lead to changes in the quantum yield of the signalling state of the protein [1]. We describe new broadband cavity enhanced absorption spectroscopy, BBCEAS, and broadband cavity ring down spectroscopy, BBCRDS [2], methods that can measure magnetic field effects on the radicals with a step change in sensitivity compared to previous transient absorption methods, at significantly lower laser powers that also reduce photodegradation. We present BBCEAS MARY curves for the photoexcited DmCry protein which show unprecedented sensitivity and reveal how these methods could be used for determining magnetic field effects at geomagnetic fields strengths in biological samples.

This poster describes the detection of a magnetic field effect on the photochemical yield of a flavin-tryptophan radical pair in *Dm*Cry, using the BBCEAS techniques. This represents the first application of BBCEAS to studying MFEs in biological systems, and, crucially, has permitted the first MFE detection on an animal protein.

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Magnetic effects on the flavin based photo-catalytic oxidation of benzyl alcohol

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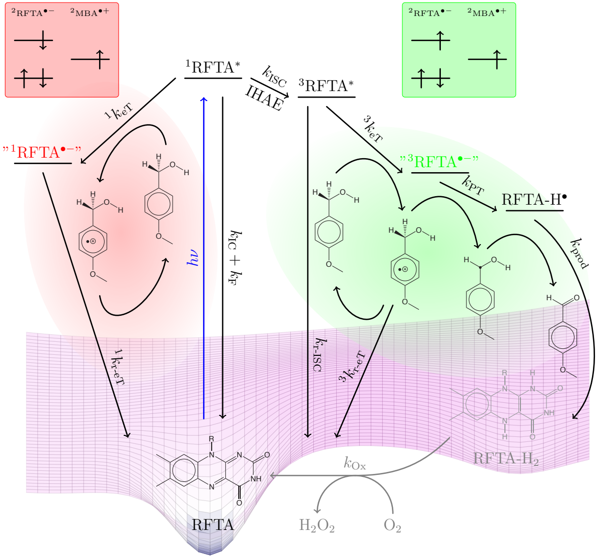
In various theoretical and experimental works on radical pair reactions it has already been shown that by external magnetic fields in the mT range the reactivity and thus the yields of potential products can be affected significantly. In this work we extend the existing principles of the magnetic field effect on photocatalytic reactions. One prominent photocatalyst, which is also used by nature, is flavin. Flavins photo-catalyze e.g. the oxidation of benzyl alcohols, benzyl amines, methylbenzenes, styrenes and phenylacetic acids by dissolved oxygen 1. Recently, we have investigated the mechanism of oxidation of benzylic alcohol to its corresponding aldehyde [2,3].



The bottle neck in this photo catalytic cycle is the formation of ionic spin correlated radical pairs (SCRP) after electron transfer from benzylic alcohol either to the excited singlet or triplet state of the flavin. The ionic singlet SCRP is formed within some ps and recombines almost as fast back into the ground state species. Instead the ionic triplet SCRP can react further on by an proton transfer forming the neutral triplet SCRP. Following this route it ends in the formation of the final product while the reduced flavin is back oxidized by dissolved oxygen. Now we could show that application of an external magnetic field of 145±3 mT affects the reactivity of the relevant SCRP $^{1,3}[^2F^{\bullet-} \cdots {}^2A^{\bullet+}]$ resulting in an increased overall product yield.

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Influence of structure on the rate constants of reversible electron transfer in oxidized peptides containing tryptophan and tyrosine

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Long-range electron transfer between tryptophan and tyrosine residues in oxidized proteins continiously arouses research interest because of its important biological implication. The examples of biological systems where electron transport involving tryptophan and tyrosine resudues is important are DNA photolyase, bovine serum albumin, hen egg white lysozyme, and others.

This work was undertaken with the aim to perform a quantitative analysis of the influence of molecular structure on the reversible intramolecular electron transfer (IET) in oxidized peptides containing tryptophan and tyrosine at acidic conditions:

$$\text{TrpNH}^{+\bullet} + \text{TyrOH} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{TrpNH} + \text{TyrO}^{\bullet} + \text{H}^{+}$$

Application of the method of time-resolved Chemically Induced Dynamic Nuclear Polarization (TR CIDNP) earlier made it possible to extract the rate constants of IET in both directions, k_f and k_r, in oxidized Trp-Tyr: $k_f=5.5\times10^5$ s^{-1} and was found to be pH-independent, k_r is proportional to proton concentration [1]. In the present study, to reveal the influence of the positive charge of terminal amino group, and the influence of spacer, glycine, on the rate constants of the reactions under study, the data for Tyr-Trp, for N-acetyl derivatives of Trp-Tyr and Tyr-Trp, and for tripeptides Trp-Gly-Tyr and Tyr-Gly-Trp were obtained. The CIDNP kinetics detected in photoreactions of photosensitizer, 2,2′-dipyridyl with the above mentioned peptides proved to be very sensitive to the rate constants of IET and made it possible to obtain the values of k_f and k_r. The work demonstrates high potential of TR CIDNP in determination of radical reaction mechanisms and absolute rate constants.

Acknowledgement. This work was supported by the program of the Russian Government “Measures to Attract Leading Scientists to Russian Educational Institutions” (grant No.11.G34.31.0045), RFBR (projects No. 11-03-00296, 13-03-00437-a), Program of Division of Chemistry and Material Science RAS (project 5.1.1), the program of the President of Russia to support the leading scientific schools (No. NSch-2429.2012.3).

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Optical Cavity-Based Detection of Magnetic Field Effects in Condensed Phase Biological Systems

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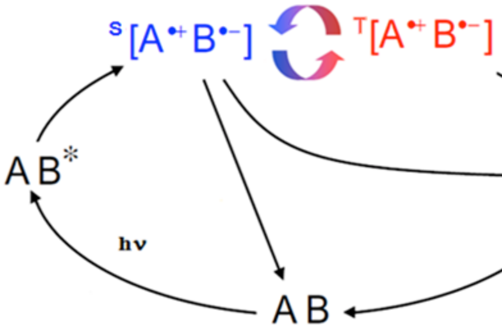
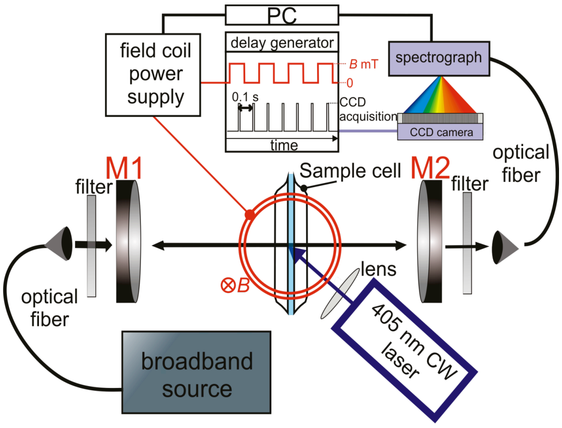
The underlying physical mechanisms of magnetosensitivity in animals remain unclear, in part due to the lack of suitable techniques for detecting the tiny effects of magnetic fields on biological systems in solution. Experiments investigating magnetic field effects (MFEs) are typically based on optical spectroscopy and have traditionally used flash-photolysis transient absorption techniques to detect short-lived radical species. Such existing methods are hampered in application to real biological systems by their requirement for large sample volumes (cm^3), high precursor concentrations (>µM), and high photolysis pulse energies, which lead to problems of photo-degradation.





We are developing sensitive optical techniques to detect MFEs in precious biological samples. The technique introduced here, condensed-phase broadband cavity enhanced absorption spectroscopy (BBCEAS), utilises supercontinuum radiation to provide simultaneous spectral information over hundreds of nanometres, encompassing entire absorption bands. The associated sensitivity gains arise from an increase in optical path length, when the light circulating in the cavity makes multiple passes through an intracavity sample. MFE studies using BBCEAS in real biological systems, including cryptochromes, have been performed.

Effect of glycerol concentration on structure of the photo-induced charge-separated state in protein:9,10-Anthraquione-1-Sulfonate bound to Human Serum Albumin

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In the photosynthesis and the DNA restoration, proteins play a crucial role on the light-energy conversions to generate reaction intermediates that transfer the electrons. Therefore it is important to elucidate conformations of the reaction intermediates in the proteins. We reported time-resolved electron paramagnetic resonance (TREPR) spectra of the photo-induced charge-separated (CS) states generated by the light excitation of a molecule bound to a protein[1]. For analysis of the protein samples at a low temperature, glycerol is normally added to the protein solutions. It is thought that glycerol molecules prevent the protein denaturation. However it is not well known how the glycerol molecules affect the conformation and the hydration structure of proteins. In this study, we prepared samples of 9,10-anthraquinone-1-sulfonate ($AQ1S^-$) bound to human serum albumin and elucidated effects of glycerol concentration on the CS structure using the TREPR method.

Glycerol and HSA-$AQ1S^-$ aqueous solution were mixed (volume ratio = 5:5 and 3:7). Concentrations of HSA and of $AQ1S^-$ were 3 mM for both solutions. Figure 1 shows TREPR spectra for different glycerol contents measured at T = 100 K. These signals were constituted by peaks of $AQ1S^{2-\cdot}$ (341 mT) and of tryptophan radical cation ($Trp^{+\cdot}$) around 342 mT. Thus, these signals were identified as the photo-induced CS state generated by the electron transfer from Trp to the excited triplet $AQ1S^-$.[1] In Figure 1, the solid line is sharper than the dot line. This difference in the line shape indicates that the orientational structure in photo-induced CS state is changed by the glycerol concentration. It is speculated that the protein strucure is influenced by the hydration strucuture change. We have determined the molecular geometris of CS state by using the triplet precursor spin-correlated radical pair model.

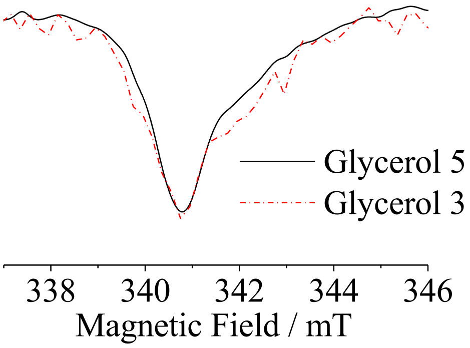

Figure 1. Effect of glycerol volume-content on the TREPR spectrum

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DEER studies of molten globule state α-lactalbumin

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Human α-lactalbumin (α-LA) is a 14 kDa, two-domain ($\alpha + \beta$), Ca^{2+}-binding protein which acts as a regulatory component of the lactose synthase enzyme. The α-domain is largely helical in the native state whereas the β-domain has a significant β-sheet content. α-LA forms a partially folded molten globule at low pH, retaining native-like secondary structure and a compact overall fold but lacking in fixed packing interactions, resulting in an interconverting ensemble of tertiary structures. There is significant interest in the molten globule state with regards to protein folding[2], and attempts to characterise it have to date used circular dichroism[3] and NMR[4].

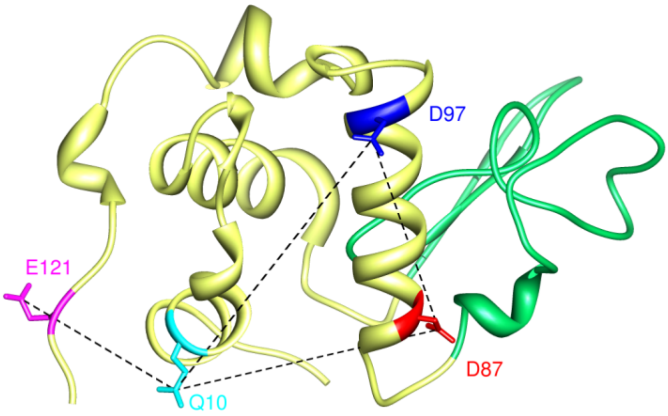

Figure 1. Human α-lactalbumin showing spin-labelled residues.[5]

A variant of α-LA in which all eight cysteines were mutated to alanine (all-Ala) has been shown to form a compact molten globule, despite the absence of the native disulphide bonds[4]. This variant provides the ideal blank canvass for the re-introduction of free cysteines, and was used to create double mutants Q10C/D87C, Q10C/D97C, D87C/D97C, and Q10C/E121C, as well as single mutants Q10C, D87C, D97C, and E121C (Figure 1). These were spin-labelled with MTSL and distances were measured by four-pulse DEER. Data were analysed in DEER-Analysis. Measured distances support retention of significant structure in the molten globule, including the close interaction of N- and C- termini seen in the native state.

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Application of Spin Chemistry Ideas in Semiconductor Spintronics Spin Filtration

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Spintronics is the spin based electronics using electron or nuclear spins (instead of charges) as information carriers [1,2]. The semiconductor spintronics should has effective sources of the spin polarized current. Spin filtration is the effective way to produce the spin current in nonorganic as well as in organic semiconductors. Unpolarized paramagnetic centers (impurities, defects, dislocations, etc) are shown can "feel" the electron spin orientation and selectively transfer their carriers from the conductivity band to the valence one. The primary process – capture of electrons by paramagnetic centers – is spin selective one and similar to spin dependent processes in radical pairs [3].

Macroscopic manifestations of spin-selective trapping of conduction-band electrons by paramagnetic centers with spin $S = 1/2$ have been studied theoretically [4]. The trapping was assumed to be possible from singlet exchange-coupled pairs "paramagnetic center-electron" only. The spin density matrix method is used to obtain the system of nonlinear algebraic equations that describe dependences of stationary densities and polarizations of electrons and paramagnetic centers. Trapping of unpolarized electrons is capable to produce strong spin polarization of paramagnetic centers. Spin selective electron trapping was shown can alter the photoconductivity of a semiconductor and influence the degree of circular polarization of luminescence. Peculiarities of transient and pulse regimes and manifestations of quantum Zeno effect in semiconductor spin dependent processes will be also discussed.

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Steady-State and Time-Resolved EPR Investigation of Nanostructures formed by Catanionic Mixtures of SDS/DTAC

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The physical properties of nanostructures formed from a mixture of oppositely charged surfactants, dodecyl trimethyl ammonium chloride (DTAC) and sodium dodecyl sulfate (SDS), are examined by steady state (SSEPR) and time-resolved electron paramagnetic resonance spectroscopy (TREPR). A micelle to vesicle transition occurs as the mixing ratio of the two surfactants approaches equimolar. SSEPR is sensitive to the diffusional motion of spin probes included inside surfactant nanostructures. Changes to the spectral lineshape can be simulated using nonlinear least square fitting method based on the stochastic Liouville equation and are indicative of decreasing rotational correlation times and increasing order of the surfactant nanostructure that correlates with the phase transition of the catanionic mixture. TREPR is sensitive to the diffusional motion of radicals inside the nanostructure. Photo-induced hydrogen atom abstraction occurs between a benzophenone, a hydrophobic triplet sensitizer, and the alkyl chain of the surfactants to generate a spin correlated radical pair that is confined by the nanostructure. The observation of the spin correlated radical pair and the EPR signal from the alkyl radicals varies substantially with the mixing ratio of SDS and DTAC. These observations can be understood in relation to the increased packing of surfactant alkyl chains and nanostructure size as a function of the surfactant mixing ratio.

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Orientational structure and charge dissociation of photoinduced charge-separated states in P3HT-PCBM blend films fabricated by the spin coating method

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Blend films composed of the conjugated polymer of poly(3-hexylthiophene)(P3HT) and the fullerene derivative of [6,6]-phenyl-C_{61}-butyric acid ester (PCBM) have attracted attention as a model system for the study of photoactive layer in bulkheterojunction organic thin-film solar cell. Only one study has directly characterized the orientation of photoinduced charge-separated (CS) state at the domain interface of blend films[1]. The mechanisms of photoelectric conversion functions have not fully been understood. In this study, we have directly observed the photoinduced CS state for the P3HT-PCBM blend films fabricated by the spin-coat method using time-resolved EPR to characterize the orientational structure and the charge-dissociation dynamics of the photoinduced CS state.

P3HT-PCBM blend films (Weight ratio was 1:1) were fabricated by the spin coating method (3000 rpm, 30 s). The thermal annealing effect was observed by using UV-Vis absorption spectra and time-resolved EPR. It was found that annealed film improved crystalinity of the P3HT domain by comparison of data from UV-vis absorption spectra. Figure 1 shows TREPR spectra of non-annealed film measured at T = 77 K. The signals were explained by the spin correlated radical pair model from the polarization pattern and the resonant magnetic field determined by the g-factor of P3HT polaron and PCBM anion as previously reported[1], denoting the photoinduced CS state generated by the electron transfer from the excited singlet P3HT to the PCBM. An A/E/A/E pattern has been appeared at the later delay time and is explained by the effect of the triplet charge recombination. We have determined the molecular geometris of CS state by using the singlet precursor spin-correlated radical pair model.

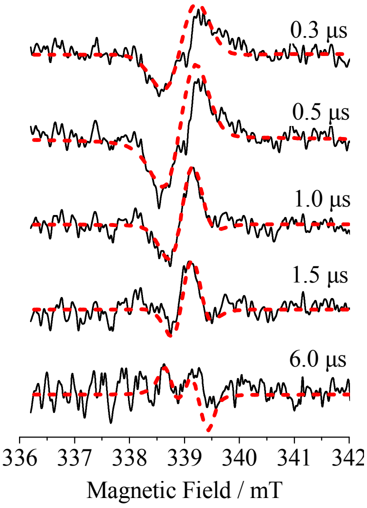

Figure 1. TREPR spectra of P3HT-PCBM blend film fabricated by the spin coating mehod.

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Spin Relaxation Times of Photoinduced Radicals in PCBM:P3HT Composite Revisited by Electron Spin Echo Technique

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The composite of [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3TH) is well known example of perspective material for active layer of organic solar cells. After light absorption the charge transfer occurs at this material leading to formation of spin-correlated pairs $PCBM^-/P3HT^+$ which can be further separated to free radicals.

In this work the spin dynamics of photoinduced radicals $PCBM^-$ and $P3HT^+$ was investigated by electron spin echo (ESE) technique at temperature 80K. The radicals were generated by visible continuous light illumination or by laser flashes. The echo-detected (ED) EPR spectrum lineshape obtained after laser flashes is strongly dependent on delay after laser flash (*DAF*). At short *DAF* values (*DAF* < 30 s) both microsecond-living spin-correlated radical pairs $PCBM^-$ /$P3HT^+$ and free long-living non-coupled radicals $PCBM^-$ and $P3HT^+$ contribute in ED EPR spectrum [1].

The transversal relaxation times T_2 were determined from ESE decays in mw pulse sequence $\pi/2$ - τ - π - *ESE*. For non-coupled radicals $PCBM^-$ and $P3HT^+$ generated by continuous light $T_{2,e} = 2.0 \pm 0.1$ μs and $T_{2,h} = 1.6 \pm 0.1$ μs were obtained, respectively. T_2 of spin-correlated radical pair $PCBM^-$ /$P3HT^+$ was about two times smaller than the T_2 values of non-coupled radicals. The model of instantaneous diffusion in ESE explains the effect of transversal relaxation time decreasing for spin-correlated radical pairs $PCBM^-/P3HT^+$. It assumes that mw pulse sequence affects both spins in the pair simultaneously. From the obtained transversal relaxation rates difference the strength of magnetic interaction in spin-correlated radical pairs $PCBM^-/P3HT^+$ was estimated as 1 MHz.

The work was supported by RFBR grants No12-03-31190-mol-a, and No12-03-00238-a.

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Temperature Dependence of Magnetophotoconductance of Hexabenzocoronene Self-Assembly

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One-dimensional photoconductor is a key material to realized ultra high efficient organic solar cell. Using transient magnetophotoconductance (MPC) measurement, in this paper, we investigated photocarrier dynamics in one-dimensional columnar assembly of hexabenzocoronene (HBC-C14) of Fig. 1, which forms highly ordered columnar stacks because of the strong π–π interactions [1]. Nanosecond time-resolved MPC measurements were performed using an integrating circuit, an electromagnet and a nanosecond YAG laser [2].

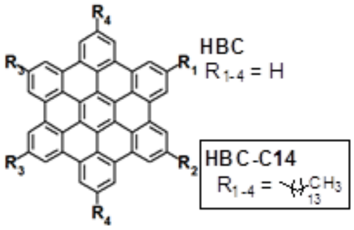

Fig. 1 Molecular structures of HBC attached with six dodecyl chains (HBC-C14).

Fig. 2a shows a typical time-profile of photocharge (Q) of HBC-C14 film observed at 200 K. A prompt signal (Q_p) was detected immediately after the flash and then the signal increased slowly with the delay time (t). The Q_p is ascribed to the initial quantity of photocarrier born though the carrier generation. The slow rising component (Q_d) arises from the carrier drift motion under the E-field corresponding to the carrier transport. With decreasing temperature (T) the intensity of Q signal decreased. Fig 2b depicts transient MPC effect ($[Q(B,t) - Q(0,t)]\times 100/Q(0,t)$) detected at magnetic field (B) of 50 mT. The Q_p component showed negative MPC, indicating dynamics of the geminate electron-hole (e-h) pair born from the singlet exciton. On the other hand, the MPC effect positively increased with the delay time (t). The time variation of MPC was interpreted in terms of the selective recombination of non-geminate e-h pair. On the basis of the T-dependences MPC, we will discuss about the mechanism for photocarrier dynamics.

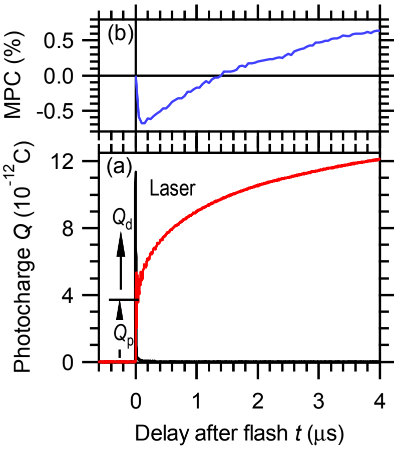

Fig. 2 Time profile of the photocharge (a) and MPC at 50 mT (b) for HBC-C14 self-assembly observed at 200 K under the electric field of 2.0×10^5 V/cm.

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Searching for Low Field Anisotropy

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It has long been known that birds are able to navigate in the earth's magnetic field. One current hypothesis for the chemical mechanism underlying this ability is the Radical Pair Mechanism. This mechanism holds that magnetic fields can influence the kinetics of a radical pair reaction, causing a change in reaction rate or product yield.

For this effect to be useful as a compass, the magnetic response must show anisotropy – that is, it must be sensitive to not only the strength, but also the direction of the magnetic field. Previous work has shown that there is a chemical compass system – a Carotenoid-Porphyrin-Fullerene Triad – which shows both a magnetic field effect at the earth's magnetic field strength, and also an anisotropic magnetic field effect at higher fields. However, the field strength at which the anisotropic effect is observed is many times the field strength of the earth's magnetic field.

The radical pair mechanism gives rise to two separate types of magnetic field effect, with opposite polarities. Of these, the Low Field Effect operates at small field strengths. It seems that, for the birds' compass to work in magnetic fields as small as the earth's, it must operate in this low field effect region. An anisotropic field effect has yet to be observed in the low field region.

This poster will look at what steps the group is taking to understand how anisotropic magnetic field effects arise, how we can accurately probe them, and how we hope to observe an anisotropic magnetic field effect in the low field region.

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CONFERENCE SCHEDULE SCM2013

	SUNDAY 21.04	MONDAY 22.04	TUESDAY 23.04	WEDNESDAY 24.04	THURSDAY 25.04
8h00		Reception Opening			
9h00		PL 1 Naaman IT 1 Woodward	PL 2 Levitt IT 11 Lukzen	PL 3 Wasielewski IT 17 Van der Est	PL 5 Takui IT 18 Cavagnero
10h00		Photo + Coffee break IT 2 Schleicher	Coffee break CT 3 Steiner	Coffee break CT 8 Yurkovskaya	Coffee break IT 19 Kobori
11h00		IT 3 Maeda IT 4 Phillips	CT 4 Borovkov CT 5 Khramtsova	CT 9 Vieth PL 4 Ehrenfreund	IT 20 Behrends CT 10 Kothe
12h00		CT 1 Carmieli Lunch break	CT 6 Miura Lunch break	Salzburg Excursion	CT 11 Koptyug Lunch break
13h00					
14h00					
15h00		IT 5 Mackenzie IT 6 Jones	IT 12 Solov'yov IT 13 Ivanov		PL 6 Coey IT 21 Flatté
16h00		IT 7 Timmel Coffee break	CT 7 Shushin Coffee break		Coffee break CT 12 Tiersch
17h00	Reception & get together	IT 8 Fedele CT 2 Biskup IT 9 Cai	IT 14 Murai IT 15 Vinogradov		IT 22 Bobbert CT 13 Das
18h00		IT 10 Matysik Dinner	IT 16 Forbes Memorial Lecture		IT 23 Basu Closing
19h00			Dinner		Dinner & Poster session
20h00		Poster session (odd numbers)	Poster session (even numbers)		
21h00					
22h00					