



Colloquium Announcement

of the Collaborative Research Centre 951

“Hybrid Inorganic/Organic Systems for Opto-Electronics”

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Photoinduced Charge Separation and Recombination in Triarylamine- Naphthalenediimide Dyads and Triads

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Operating Molecular Photoswitches by Oxidation/Reduction

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Place: Erwin-Schrödinger-Zentrum, Rudower Chaussee 26,
Room 0'119.



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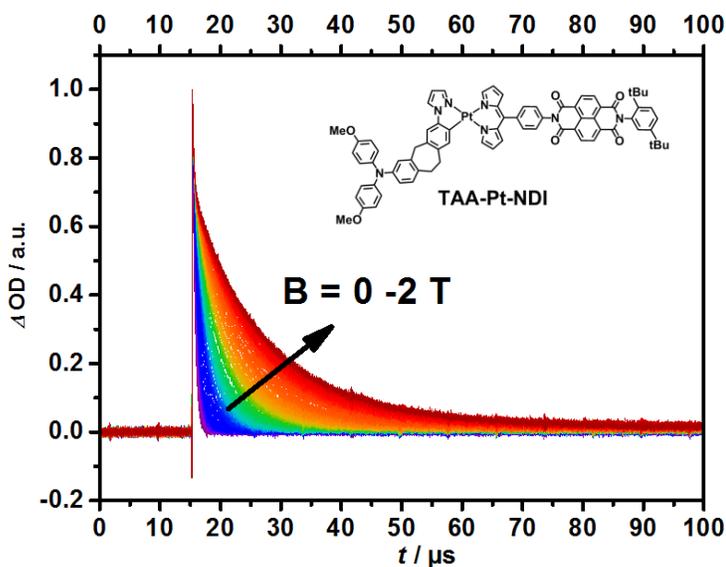
Photoinduced Charge Separation and Recombination in Triarylamine-Naphthalenediimide Dyads and Triads

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



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

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

References

[1] J. H. Klein, D. Schmidt, U. E. Steiner, C. Lambert, *J. Am. Chem. Soc.* 137, 11011-11021 (2015).

[2] J. H. Klein, T. L. Sunderland, C. Kaufmann, M. Holzapfel, A. Schmiedel, C. Lambert *Phys. Chem. Chem. Phys.* 15, 16024-16030 (2013).

Operating Molecular Photoswitches by Oxidation/Reduction

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Photoswitches are useful molecular building blocks to implement in hybrid inorganic/organic materials and devices in order to attain optical control over their properties. While photochromism research has traditionally been concerned with the photochemistry of these compounds, we have recently uncovered intriguing electrochemical behavior as well. In depth spectroelectrochemical investigations in combination with computational studies show that thermal barriers between (meta-stable) switching states are largely altered upon oxidation and/or reduction of the molecules. Accelerated isomerization of the radical ion intermediate can be followed by a facile electron transfer to another switch molecule, thereby giving rise to a catalytic and hence highly efficient alternative switching pathway (*J. Am. Chem. Soc.* **2017**, *139*, 335-341). These results are important in the context of constructing switchable hybrid interfaces. Selected examples, including pyridine and poly(para-phenylene) on ZnO and others, will show how we explore, control, and predict level alignment and light-matter interaction at hybrid interfaces.