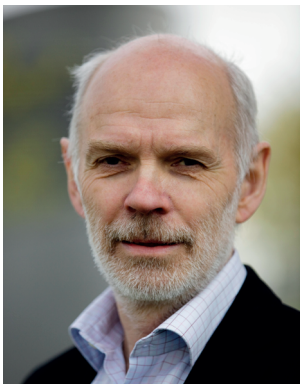
Excited by Light | Nordic Femtochemistry XII



Mikael Risedal

Jens Uhlig

The “Excited by Light” international symposium is organised in honour of Prof. Villy Sundström's lifetime achievements in science. We have invited several prominent speakers whose scientific activities in femtochemistry, femtobiology and solar energy conversion overlap with the broad research areas where Villy Sundström has made important contributions. It is our hope that this symposium will bring together leading experts from these different research areas in order to promote cutting edge science and provide a forum for interdisciplinary discussions which are all “excited by light”!

Nordic Femtochemistry XII aims to bring the Nordic and Baltic femtoscience communities together in order to establish new connections and share the latest results and ideas. The conference has a wide scope which encompasses a broad range of ultrafast phenomena in chemistry, physics and biology
Several prominent members of the femtoscience community have been invited to share their recent contributions to the field.

Organizing Committee

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Monday, 23.05.2016			
0900 – 1230	Arrival & Registration		
1230 – 1350	Lunch		
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1400 – 1430	Graham Fleming University of California, Berkeley, USA	Complex Dynamics from Molecules to Membranes	I1
1430 – 1500	Sune Svanberg Lund University, Sweden	Laser Spectroscopy Applied to Environmental, Ecological, Food Safety, and Biomedical Research	I2
1500 – 1530	Lars Samuelson Lund University, Sweden	From Nanowire-Based Solar-Cells Excited by Light to Nanowire-LEDs Excited by Electrons	I3
1530 – 1600	Thomas Elsaesser Max Born Institute, Berlin, Germany	Structure Fluctuations and Short-Range Electric Interactions of Hydrated DNA Mapped by 2D Infrared Spectroscopy	I4
1600 – 1630	Refreshment Break		
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0900 – 0930	Leonas Valkūnas Vilnius University, Lithuania	Modeling of Self-Regulation Ability of Light-Harvesting Antenna	I9
0930 – 1000	Oliver Kühn Rostock University, Germany	Quantum Dynamics of Excitons in Natural and Artificial Light-Harvesting	I10
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1030 – 1100	Rienk van Grondelle Free University, Amsterdam, Netherlands	How Exciton-Vibrational Coherences Control Charge Separation in the Photosystem II Reaction Center	I11
1100 – 1130	Alfred Holzwarth Max-Planck-Institute for Chemical Energy Conversion, Mülheim a.d. Ruhr, Germany	Quantum Biology in Action: The Chlorosome Antenna of Green Bacteria	I12
1130 – 1200	Neil Hunter University of Sheffield, UK	Native and Fabricated Membrane Protein Architectures for Energy Transfer and Trapping	I13
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1400 – 1430	Leif Hammarström Uppsala University, Sweden	Capturing Intermediates of Molecular Solar Fuels Catalysts by Femto- and Nanosecond Mid-IR Spectroscopy	I15
1430 – 1500	Jouko Korppi-Tommola University of Jyväskylä, Finland	Intriguing Photochemistry of the Additives in the Dye-sensitized Solar Cells	I16
1500 – 1530	Arvi Freiberg University of Tartu, Estonia	Remarkable Robustness of Photosynthetic Exciton Polarons Against Physical Stress – Temperature and Pressure	I17
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0920 – 0940	Heli Lehtivuori University of Jyväskylä, Finland	Electron Transfer Reactions in Bacteriophytochrome Proteins	O2
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1120 – 1140	Matthijs Panman University of Gothenburg, Sweden	Direct Visualization of Fundamental Reaction Events in Solution with Femtosecond Time-Resolved Wide-angle X-Ray Scattering	O5
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1410 – 1430	Wei Zhang Lund University, Sweden	Carrier Recombination Processes in Indium Gallium Phosphide Nanowires	O8
1430 – 1450	Kati Stranius Tampere University of Technology, Finland	Photophysical Study of a Self-Assembled Donor-Acceptor Two Layer Film on TiO_2	O9
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1610 – 1630	Erling Thyrhaug Lund University, Sweden	Ultrafast Dynamics in DNA Templated Silver Clusters	O11
1630 – 1650	Erik Mårsell Lund University, Sweden	Spatiotemporal Imaging of Few-Cycle Nanoplasmonic Fields Using Photoemission Electron Microscopy	O12
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0920 – 0940	Quentin Daniel Royal Institute of Technology, Sweden	Cobalt-Porphyrin for Water Oxidation on FTO Surface, Molecular or Metal Oxide Catalyst?	O15
0940 – 1000	Aboma Merdasa Lund University, Sweden	Nature of Photogenerated Quenchers in Methylammonium Lead Iodide Perovskites Revealed by Temporally and Spatially Resolved Photoluminescence	O16
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1050 – 1110	Vladimir Osipov Lund University, Sweden	Detection of Kinetics Type from Action Signals of Phase Modulated Light Fields	O18
1110 – 1130	Matyas Papai Technical University of Denmark, Denmark	Controlling the Photoexcited Decay of Fe(II)-N-Heterocyclic Carbene Complexes Through Structural Modifications	O19
1130 – 1150	Lisa Fredin National Institute of Standards and Technology	Untangling Light Induced Decay Pathways of Iron-Carbenes using Theory	O20
1150 – 1200	Closing Remarks		
1200 – 1320	Lunch		
1320	Departure		

I1

Complex Dynamics from Molecules to Membranes

Graham R. Fleming

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Two Dimensional Electronic Spectroscopy has enabled many new insights on systems ranging from carbon nanotubes to photosynthetic light harvesting complexes. But it also is generally not well enough resolved to reveal the role and influence of nuclear degrees of freedom (vibrations) in molecular dynamics. To address this issue we developed two-dimensional electronic vibrational spectroscopy (2DEV) where the correlation of the electronic evolution with that of the nuclei is measured. I will illustrate the power of 2DEV spectroscopy with a range of examples including energy flow in LHCII, the major light harvesting complex of green plants.

Taking the kind of microscopic information described above (10s – 100s fs timescale; 1nm lengthscale) and applying it to examine the functional behavior of the thylakoid membrane of a chloroplast requires building multiscale models that should, in principle, extend the timescales up to minutes or hours and the lengthscale to microns. I will describe a multiscale model that successfully describes energy flow on the 300nm x 300nm lengthscale and 100s of ps timescale. If time permits, I will describe how introducing non-photochemical quenching into the model informs ways of analyzing fluorescence data on plants adapting to changes in light intensity.

I2

Laser Spectroscopy applied to Environmental, Ecological, Food Safety, and Biomedical Research

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Laser spectroscopy provides many possibilities for multi-disciplinary applications in environmental monitoring, in the ecological field, for food safety investigations, and in biomedicine. Several examples of the power of multi-disciplinary applications of laser spectroscopy are given. The applications utilize mostly similar and widely applicable spectroscopic approaches. Air pollution and vegetation monitoring by lidar techniques, as well as agricultural pest insect monitoring and classification by elastic scattering and fluorescence spectroscopy are described. Biomedical aspects include food safety applications and malaria diagnostics. Non-invasive monitoring of sinusitis and otitis is further described, with strong connection to the abatement of antibiotics resistance development. Finally, the techniques have strong impact also on the surveillance of the smallest patients – prematurely born children.

The author is very grateful for a much rewarding collaboration with numerous colleagues and students. This work was supported by the Swedish Research Council, The Knut and Alice Wallenberg Foundation and the Guangdong Province Innovation Team Program (201001D0104799318).

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5. S. Svanberg, G.Y. Zhao, H. Zhang, J. Huang, M. Lian, T.Q. Li, S.M. Zhu, Y.Y. Li, Z. Duan, H.Y. Lin and K. Svanberg, Laser Spectroscopy Applied to Environmental, Ecological, Food Safety and Biomedical Research, Optics Express **24**, A515 (2016)

I3

From Nanowire-based solar-cells excited by light to Nanowire-LEDs excited by electrons

L. Samuelson

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I will here present research that has been developed within NanoLund/nmC, in the general area of Nano-Energy that for the last ten years has been coordinated by Villy Sundström. Semiconductor nanowires are 'needle'-like structures with unique materials, electronic and optical properties that renders them promising for next-generation applications in fields like opto/electronics, energy systems and life sciences. An intensive and world-wide research effort in the field of nanowires was launched in the late 1990s, about ten years after the pioneering work by Dr. Hiruma at Hitachi, Japan. In my research group we spent the first five years on fundamental studies of the materials growth and the materials physics of nanowires, especially heterostructure systems (*1*), while in parallel also developing novel methods that combined top-down patterning with bottom-up self-assembly, to enable the reproducible fabrication of perfectly ordered nanowire arrays (*2*), (*3*).

From around 2005 it became evident that this blue-sky materials research (*4*), (*5*) offered significant advantages and opportunities for various applications, primarily in enabling high-speed (*6*) and optoelectronics devices by monolithic integration of III-V nanowires with silicon (*7*). We have also explored ways in which these nanostructures can be used for energy scavenging (*8*) and in applications that enable energy conservation (*9*).

In this talk I will also present my perspective of broader materials research considerations related to semiconductor nanowires, what the state-of-the-art is, what the key challenges are and focus particularly on the opportunities that these nanostructures present in terms of realizing the next-generation of high-performance optoelectronics devices such as solar cells and light-emitting diodes, at a low cost and with low materials consumption (*10*).

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I4

Structure Fluctuations and Short-Range Electric Interactions of Hydrated DNA Mapped by 2D Infrared Spectroscopy

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The interface of DNA with its hydrating water shell is characterized by a complex interplay of electric forces and hydrogen bonding among water dipoles, counterions and the charged and polar groups of the double helix. The structure of the water shell fluctuates on a multitude of time scales with the fastest molecular motions in the femtosecond time domain [1-3]. Utilizing vibrational modes of the backbone of short double-stranded DNA oligomers, femtosecond 2D infrared spectroscopy has given insight in thermal equilibrium fluctuations and non-equilibrium energy transfer processes at the interface [4,5]. Here, new results for a natural DNA sequence of up to 2000 base pairs in its native aqueous environment are presented. Step-wise dehydration allows for discerning the contributions and respective time scales of different interfacial species to the fluctuating electric forces that act on the backbone oscillators. We find that water in the first two hydration layers from the DNA surface generates the major part of electric forces, showing thermal fluctuations on a time scale of 300 fs, approximately an order of magnitude slower than bulk water. Contributions from outer water layers to the net forces acting on the DNA surface are screened and, thus, minor as is evident from 2D infrared spectra recorded at different hydration levels. The screening by water dipoles within the first two water layers is further manifested in the invariance of interfacial electric fluctuations upon switching from mono- to divalent counterions. Furthermore, the 2D infrared spectra demonstrate a quasi-static inhomogeneous broadening that reflects structural disorder of the hydrated interface and lifetimes of DNA-water hydrogen bonds beyond 10 ps. Implications of the results for describing electric interactions at hydrated charged biointerfaces will be discussed.

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I5

Excitons and charges in molecular semiconductors

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The physics of organic semiconductors is often controlled by large electron-hole Coulomb interactions and by large spin exchange energies. Photogenerated excitations are generally found to be strongly bound excitons, so that operation of an organic photovoltaic diode requires a donor-acceptor heterojunction that can split a photogenerated exciton to an electron-hole pair. In order to achieve long range charge separation it is necessary to to move these charges beyond the range of the Coulomb interaction between electron and hole, a distance of 5 nm or more. We have found that it is possible to measure the Coulomb energy set up as the electron-hole pair separate, through the modulation of the ground-state optical absorption of the donor caused by the local electric field set up between the electron and hole for a range of systems that use fullerenes as the electron acceptor [1]. We found a substantial electron-hole separation at very early times, setting up an electrostatic field energy of up to 200 meV in times as short as 40 fsecs. We consider that this arises through direct electron transfer from donor to acceptor states that are delocalised over many acceptor molecules, over distances of 4 nm or more. I will report recent work that reveals this process to be general for a range of systems including those with non-fullerene acceptors. I will report also some recent observations of the process of ionisation of triplet excitons (generated via fission of triplet pairs from photogenerated singlet excitons) at all-organic donor acceptor heterojunctions formed with pentacene, based on structures we have previously reported [2]. An alternative approach is to transfer the triplet exciton itself to a luminescent material and we have explored transfer of triplet excitons from pentacene to lead selenide nanocrystals [3].

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2 "Triplet diffusion in singlet exciton fission sensitized pentacene solar cells", M. Tabachnyk, B. Ehrler, S. Bayliss, R. H. Friend, and N. C. Greenham, Applied Physics Letters **103** (2013) 10.1063/1.4824420.

3 "Resonant Energy Transfer of Triplet Excitons from Organic to Inorganic Semiconductors", M. Tabachnyk, B. Ehrler, S. Gélinas, M. L. Böhm, B. J. Walker, K. P. Musselman, N. C. Greenham, R. H. Friend, and A. Rao, Nature Materials **13,** 1033-1038 (2014) 10.1038/NMAT4093.

I6

Optical transients and semitransparent modules: towards optimized solar energy conversion with donor/acceptor blends

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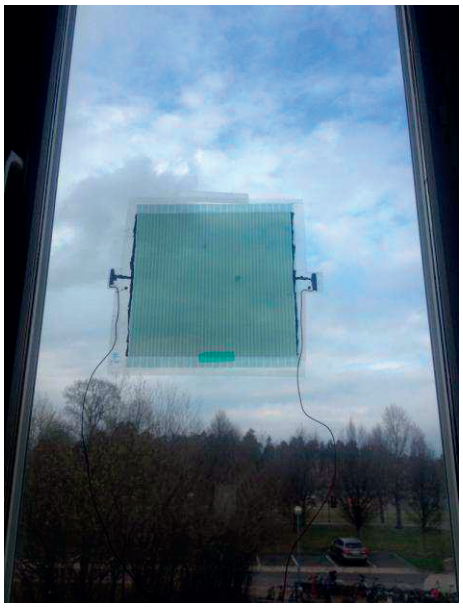
Excited states from light absorbed in organic molecules may lead to formation of charge carriers. The formation of charge carriers from dissociation of excited states into electrons and holes is critical in organic solar cells based on donor/acceptor combinations. These are topics studied over the last 20 years, in collaboration with Villy Sundström and colleagues in Lund. The use of rapid laser pulses, transient absorption and emission from charged or neutral species, and microwave reflectivity puts an experimental background for following the trace of photogenerated charges in time and space. We have unified these experimental techniques with Monte Carlo simulation of the movement of localized charges in a disordered medium. The disorder gives rise to dispersive transport, and the modeling parameters may be chosen so as to fit all transient data. This holds true for one special system, the blend of TQ1/PCBM.

Similar blends are now being used in semitransparent photovoltaic modules, printed with a prototype printer on plastic foil. Many of the problems of upscaling from mm^2 solar cells to m^2 solar modules remain, but quite a few have been solved. The moderate energy conversion efficiency of present generations of semitransparent printed organic photovoltaics is compensated by the rapid energy payback time, due to the use of very thin layers of active materials.



Another sunny day in Linköping!

I7

Me and my friend Villy

Richard Cogdell, University of Glasgow, UK

This lecture will concentrate of telling the story of how ideas on the mechanisms of energy transfer in purple photosynthetic bacterial light harvesting complexes required the combination of structural biology and time-resolved laser spectroscopy. I will particularly highlight the role Villy and his group have played in this story both when he was in Umea and later in Lund.

Coherent Ultrafast Multidimensional Spectroscopy of Molecules with Optical, X-ray, and Quantum Light

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Multidimensional spectroscopy uses sequences of optical pulses to study dynamical processes in complex molecules through correlation plots involving several time delay periods. Recent extensions of these techniques to the x-ray regime as well as by utilizing the quantum nature of light will be discussed.

Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a uniquely high spatial and temporal resolution. We demonstrate how stimulated Raman detection of an X-ray probe may be used to monitor the phase and dynamics of the nonequilibrium valence electronic state wavepacket created by e.g. photoexcitation, photoionization and Auger processes. Applications will be presented to long-range charge transfer in proteins and to excitation energy transfer in porphyrin arrays.

Many important photophysical and photochemical molecular processes take place via conical intersections (COIS) where nuclear and electronic degrees of freedom become strongly coupled and the adiabatic Born Oppenheimer approximation beaks down. A new technique, TRUE-CARS, Transient Redistribution of Ultrafast Electronic Coherences in Attosecond Raman Signals, is proposed that can detect the passage through a COIS. Entangled photons provide novel nonlinear spectroscopic probes of excitation-energy-transfer and charge-separation processes in chromophore aggregates. Signals that utilize the quantum nature of the optical field by varying parameters of the photon wavefunction rather than classical field delays and frequencies will be presented. The unusual spectral and temporal characteristics of entangled photon pairs combined with interferometric detection make it possible to manipulate and control two photon absorption and Raman signals and extract information not available with classical light.

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3. *"Multidimensional Attosecond Resonant X-ray Spectroscopy of Molecules; Lessons from the Optical Regime", J. Biggs, D. Healion, Y. Zhang, and S. Mukamel. Ann Rev Phys Chem, 64, 101-127 (2013).*
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I9

Modeling of self-regulation ability of light-harvesting antenna

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The photosynthetic apparatus of green plants is well-known for its extremely high efficiency that allows them to operate under dim light conditions. On the other hand, intense sunlight may result in over-excitation of the light-harvesting antenna and the formation of reactive compounds capable of "burning out" the whole photosynthetic unit. Non-photochemical quenching (NPQ) is a self-regulatory mechanism utilised by green plants on a molecular level that allows them to safely dissipate the detrimental excess excitation energy as heat. While it is believed to take place in the plant's major light-harvesting complexes (LHCII), there is still no consensus regarding its molecular nature. To get more insight into its physical origin, high-resolution time-resolved fluorescence measurements of LHCII trimers and their aggregates are analyzed over a wide temperature range [1]. Based on simulations of the excitation energy transfer in the LHCII aggregate, we associate the red-emitting state, having fluorescence maximum at ~700 nm, with the partial mixing of excitonic and chlorophyll–chlorophyll charge transfer states. On the other hand, the quenched state has a totally different nature and is related to the incoherent excitation transfer to the short-lived carotenoid excited states. Our results also show that the required level of photoprotection *in vivo* can be achieved by a very subtle change in the number of LHCIIs switched to the quenched state.

J. Chmeliov, A. Gelzinis, E. Songaila, R. Augulis, C. D. P. Duffy, A. P. Ruban, L. Valkunas, Nature Plants, in press.

I10

Quantum Dynamics of Excitons in Natural and Artificial Light-Harvesting

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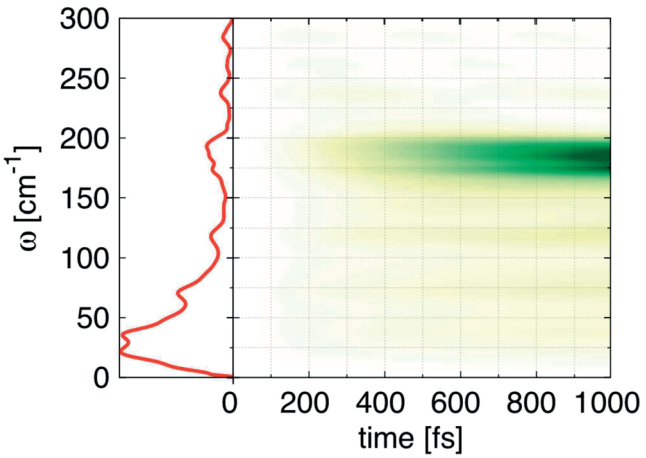
Excitation energy transfer in supramolecular architectures covers a broad range of dynamical regimes, depending on the electronic properties of the constituent dye building blocks, their mutual Coulomb interaction, as well as the coupling to vibrational degrees of freedom and to some solvent or protein environment [1]. Following the discovery of long-lived coherent oscillations in the FMO light- harvesting complex by means of two-dimensional spectroscopy, considerable attention has been paid to the role of exciton-vibrational coupling, which goes beyond that of a mere heat bath for disposing excess energy. Fortunately, with the development of the hierarchy equation of motion approach and multilayer MCTDH for the dissipative and the coherent regime, respectively, theoretical tools are available to address such dynamics in great detail. In both cases, the spectral density describing the exciton-vibrational coupling is the central quantity [2].
This presentation will focus on the spectroscopy and quantum dynamics of artificial molecular aggregates and crystals as well as of the photosynthetic FMO complex. It includes the discussion of a new protocol for the calculation of spectral densities based on the self-consistent charge tight-binding DFT method [3] and dissipative [4] as well as high-dimensional coherent [5,6] quantum dynamics simulations (see figure).



Vibronic excitation at the terminal site of the monomeric FMO complex together with the underlying spectral density of Wendling et al. (*J. Phys. Chem. B* **104**, 5825 (2000)); for details, see Ref. [5].

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I11

How exciton-vibrational coherences control charge separation in the photosystem II reaction center

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In photosynthesis absorbed sun light produces collective excitations (excitons) that form a coherent superposition of electronic and vibrational states of the individual pigments. Two-dimensional (2D) electronic spectroscopy allows a visualization of how these coherences are involved in the primary processes of energy and charge transfer. Based on quantitative modeling we identify the exciton-vibrational coherences observed in 2D photon echo of the photosystem II reaction center (PSII-RC). We find that the vibrations resonant with the exciton splittings can modify the delocalization of the exciton states and produce additional states, thus promoting directed energy transfer and allowing a switch between the two charge separation pathways. We conclude that the coincidence of the frequencies of the most intense vibrations with the splittings within the manifold of exciton and charge-transfer states in the PSII-RC is not occurring by chance, but reflects a fundamental principle of how energy conversion in photosynthesis was optimized.

I12

Quantum biology in action: The chlorosome antenna of green bacteria

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Chlorosomes are photosynthetic light-harvesting antenna structures found in green sulfur bacteria and some green filamentous bacteria. They are the largest antenna complexes in nature, measuring up to ~300-400 nm in length, 100-200 nm in width, and 20-60 nm in height. They may contain up to several 10^5 bacteriochlorophylls (BChls) *c*, *d* or *e* chromophores which are unique to chlorosomes [1]. The highly unusual property of chlorosomes is their supramolecular self-aggregates of BChls which are formed without the direct interaction with proteins as scaffolds [2,3]. The BChls are tightly packed in self-organized rod-like structures[4]. The large number of strongly interacting pigments, strong exciton delocalization[5] and ultrafast long-distance energy transfer make the chlorosome a very unusual and highly efficient light-harvesting antenna that allows the bacteria to grow phototrophically at extremely low irradiation intensities. Their exceptional exciton properties has raised interest in the chlorosome as a model system for building artificial light-harvesting nanostructures [6].

We have studied the ultrafast exciton dynamics and the dichroic optical properties of w.t. and mutant chlorosomes of *Chl. tepidum.* Evidence is presented that chlorosomes act as a huge supramolecular coherent light-harvester unit.

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I13

Native and Fabricated Membrane Protein Architectures for Energy Transfer and Trapping

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Atomic force microscopy (AFM) shows how the supramolecular organization of chlorophyll-protein complexes can bring about efficient solar energy harvesting and charge separation. Recently, computational models of whole membrane assemblies have been generated that predict energy transfer and trapping behaviour and identify desirable design motifs for artificial photosynthetic systems.

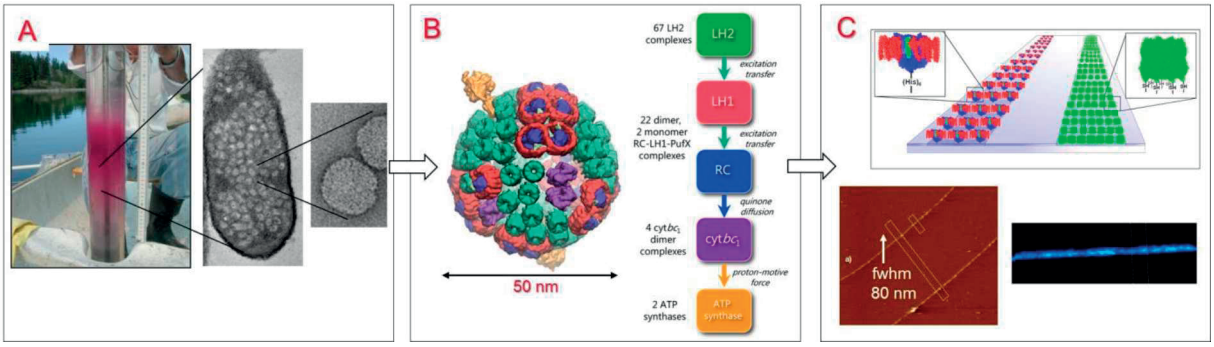

Fig. 1. A, Some photosynthetic bacteria contain hundreds of membrane vesicles that convert light to ATP. B, 1.9 million atom vesicle model derived from X-ray crystallography of the complexes and atomic force microscopy (AFM). C, (top) Concept for nanolithography to create surface-immobilised arrays of LH2 complexes (green) and dimeric RC-LH1-PufX complexes (red/blue); (bottom) AFM of an LH2 nanoline and fluorescence (inset) of 80 nm wide LH2 lines.

Nanofabrication methods allows new energy transfer geometries to be explored that are inaccessible through genetic or biochemical methods, providing test-beds for controlling and corralling energy migration. A variety of lithographic methods can be used to direct the assembly of multi-component LH and RC structures on a single surface to promote directed energy migration and trapping. Associated with this, various forms of microscopy are required for spectroscopic readout with acceptable spatial, spectral and time resolution. Finally, suitably robust biological, biohybrid and bioinspired molecules employing de novo designed maquette proteins and/or pigments have to be constructed.

This talk will present recent progress on AFM mapping and computational modelling of purple bacterial, cyanobacterial and plant membranes, and it will show how new surface chemistries and lithographic methods are being used for the 'bottom up' fabrication of integrated architectures for energy transfer and trapping.

I14

Linker design for molecule-semiconductor interfaces

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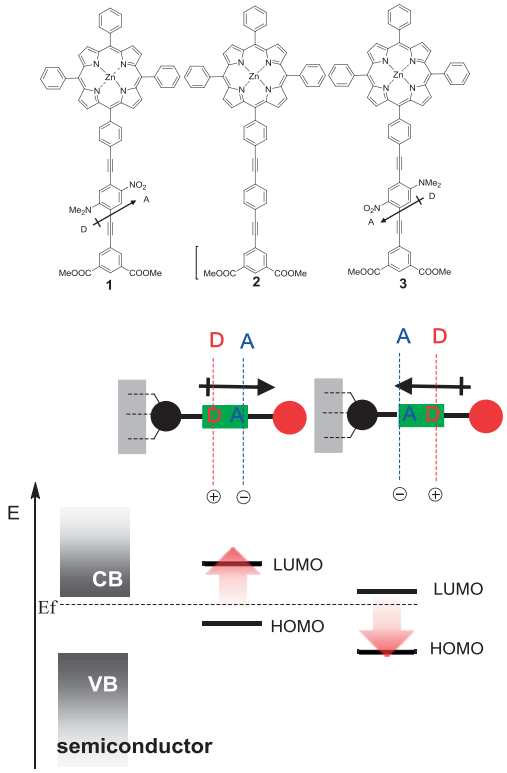
Over the past two decades molecular design has played an important role to control, at the molecular level, the properties of the interface between nanostructured metal oxide semiconductors (particularly TiO_2 and ZnO) and chromophoric compounds. The ultimate objective is develop hybrid organic-inorganic systems that are widely employed in solar photochemical energy conversion that will lead to efficient solar cells and photocatalysts, but an important aspect of this research is the ability gain a fundamental understanding of charge transfer processes at these important interfaces. The presentation will address several aspect of molecular design that our group has focused on, chromophore shielding, linker-anchor design and, in particular, our recent progress in the influence of interfacial dipoles.



I15

Capturing intermediates of molecular solar fuels catalysts by femto- and nanosecond mid-IR spectroscopy

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Molecular catalysts offer a potentially high activity and selectivity for solar fuels production. Rational design of catalysts requires mechanistic understanding beyond overall performance measurements and benchmarking. By time-resolved laser spectroscopy reaction intermediates can be identified and their rates of interconversion can be determined.

We have used a laser flash-quench method with time-resolved UV/VIS and mid-IR spectroscopy to induce rapid (~100 ns) reduction and protonation steps of [FeFe]-hydrogenase mimics. In this way we can control single-electron reduction on a short time scale, and capture reactive intermediates that are not easily accessible by e.g. electrochemical methods. From the transient mid-IR spectra and comparison with calculated spectra, we could determine the structure of several intermediates of a photocatalytic proton reduction cycle. The results also show that the photocatalytic mechanism can be different from electrocatalytic mechanisms for the same catalyst, which illustrates the need for mechanistic understanding and underscores the problem of meaningful benchmarking of catalyst performance.

The combination of ultra-fast UV-VIS and mid-IR spectroscopy is useful also to follow reaction steps of molecular dyes and catalysts immobilized on semi-conductor surfaces. We have been able to follow light-induced hole- and electron injection into the semi-conductor, ultrafast electron hopping from dye to catalysts on a NiO surface, as well as several steps in the photoreduction cycle of CO_2-reducing catalysts.

I16

Intriguing Photochemistry of the Additives in the Dye-sensitized Solar Cells

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Over the years numerous mixes of chemical compounds have been tried in the electrolytes of dye-sensitized solar cells (DSC) in efforts to improve their efficiency. How these chemicals interact with each other and the photo-electrode (PE) has received surprisingly little attention. Here we report results from a systematic study of the I^-/I_3^- electrolyte and its common additives using infrared and Raman spectroscopy together with DFT calculations. In the I_2/LiI electrolyte competing interactions between lithium cation and the MPN solvent on one hand and the additives of TBP, NMBI and GuSCN on the other hand were identified. These interactions may reduce the concentration of free lithium ions in the solutions and thereby inhibit their interactions with the TiO_2 surfaces of the PE. It was found that under Raman excitation of PMII solution in contact with the PE, efficient generation of I_3^- takes place. For the LiI solution, in addition, a I_2-dye complex is formed. The results could be explained as diffusion limited build-up of I_3^- and depletion of I^- concentrations in the focal area of the Raman excitation beam and by reduction of I_3^- via conduction band electrons of TiO_2 beyond the focal area. To explain formation of I_2-dye complexes a new multi-step dye regeneration mechanism is proposed. The effects of addition of GuSCN in the electrolytes were threefold, addition prevented the dye-I_2 complex formation in the I_2/LiI electrolyte, it decreased the amount of the photo-generated I_3^- in all cases, and it almost completely removed the Li-MPN interactions. From infrared spectra it became clear that preventing water entering the DSCs during the preparation stages in ambient air is a demanding task. The identified interactions paint an intriguing new photochemical landscape of the function of the DSCs and give support to the ultrafast regeneration mechanism proposed by us in JPCC 118 (2014) 7772.

I17

Remarkable Robustness of Photosynthetic Exciton Polarons against Physical Stress – Temperature and Pressure

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In photosynthesis solar photons are converted into molecular excitations in the antenna pigment-protein complexes and the absorbed energy is transported to the reaction center complexes, where further conversion into chemical energy occurs. The light harvesting efficiency is significantly enhanced by the inter-pigment exciton interactions present in the antenna complexes, which not only broaden their energy spectrum, but also, by virtue of building up a suitable energetic ladder of exciton states, allows ultrafast excitation energy transfer with minimal losses. Due to the established strong coupling of excitons with environmental phonons as well as a strong conformational disorder, the antenna excitons should be classified as localized exciton polarons.

Over the years, we have observed amazing robustness of photosynthetic exciton polarons to low/high temperatures as well as to low/high external pressures. A short outline of these experimental discoveries and their implication to the future development of the field will be discussed.

I18

Ultrafast carotenoid-induced quenching of excited chlorophyll in some LHC-family proteins

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All photosynthetic organisms have to cope with unpredictable changes in light intensity as over-excitation of photosystems results in generation of reactive oxygen species. To prevent this, light-harvesting complexes (LHCs) of plants and algae have an inbuilt ability to switch from light-harvesting to a quenching state in which energy is dissipated. Different molecular mechanisms involving carotenoids have been proposed to explain the principle of energy dissipation in LHCs, including energy transfer quenching (*1*) or electron transfer quenching (*2*). Recently, we demonstrated that efficient Chl quenching achieved via energy transfer from Q_y Chl-a to the S_1 state of β-carotene operates in a cyanobacterial high-light inducible protein (Hlip) forming a complex with the Ycf39 protein (*3*). Here we show that the quenching mechanism in Hlips is the same for a Hlip in a complex with the chlorophyll-synthase. In both systems, significant part of the excited Chl-a population is within 2 ps transferred to the S_1 state of β-carotene bound to Hlip. Further, we examined quenching mechanism in another member of the LHC family, the LHCSR protein from the moss *Physcomitrella patens*. Contrary to Hlips, which are essentially locked in a quenching state and the quenching is pH-independent (*3*), Chl-a quenching in LHCSR is induced by a pH change. We used LHCSR proteins containing either violaxanthin or zeaxanthin as the primary carotenoid, and we measured their transient absorption spectra in both quenched (pH 5) and non-quenched (pH 7) state. The pH-induced quenching in LHCSR is slower than the energy transfer quenching observed in Hlip. In LHCSR, a carotenoid is populated within 30-40 ps and the spectrum of the quenching product is reminiscent of a carotenoid radical cation, suggesting that the pH-induced quenching mechanism is likely electron transfer from the carotenoid to the excited Chl-a.

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I19

Controlling the flow of light on the nanoscale

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The interaction between light and matter on the nanoscale is not only fascinating, but also full of application potential. Interest in plasmonic nanostructures is sparked by the unique capabilities they possess, enabling the manipulation of the optical state of light on a sub-wavelength scale. In this talk, both passive and active control schemes are presented to explore the capture and propagation of light on spatial scales comparable to the wavelength. The nanophotonic structure we study consists of an array or pattern of holes in a gold film (see Fig. 1). Tailoring the design and/or excitation of the structure allows us to play with directional properties of the optical modes. By shaping the wavefront of the light used to excite the nanostructure we set the illumination conditions of each individual source of surface plasmons. As a result we can steer propagating plasmons and create polarization singularities. Beyond fundamental insights, this research can contribute to interesting applications for controlling the optical state of emitters, discriminating chiral molecules, or driving molecular motors.

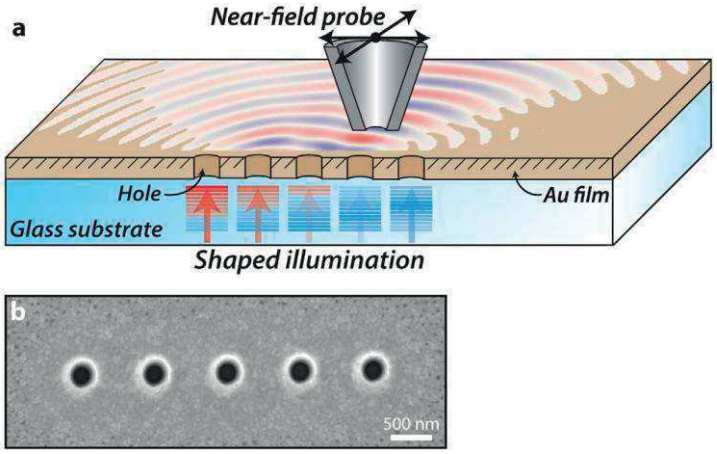

Fig.1. Hole-antenna system made in a gold (Au) film. (a) Schematic representation of the gold film with 5 holes which are illuminated from the bottom. The amplitude, phase and polarization state of each hole is controlled independently. The optical signal on the top surface is measured using a Near-field Scanning Optical Microscope. Panel (b) shows a SEM micrograph of 5 holes in a 250 nm thick Au film. From Ref. 1.

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From Purple Bacteria to Quantum Dots: an Excited Journey

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Fluorescence and photocurrent detected 2D spectroscopies (1) are relatively recent additions to the coherent multidimensional spectroscopy family of methods. Particularly the photocurrent detection allows selectivity which enables to relate the 2D spectral evolution directly to the "action" in the material of the device which is studied – photo-generated current in a solar cell or a photo-cell. The methods provide an additional excited state absorption (ESA) pathway compared to the conventional photon echo 2D signal. The 2 ESA components have opposite signs, one of them leads to singly excited, other to the doubly excited population. In molecular aggregates like light harvesting complexes the doubly excited state rapidly relaxes to a singly excited state through exciton-exciton annihilation (2). As a consequence the two ESA pathways give very similar signal amplitudes and because of the opposite signs, they take out each other.

We have earlier used fluorescence and photocurrent detected 2D spectroscopy to study multiple exciton generation in colloidal quantum dots (1). Here we are presenting fluorescence detected 2D spectroscopy study of excitons and their dynamics in LH2. Since the ESA signal is negligible, the cross peaks of the 2D spectra are very clear showing partial inter-band delocalization of the excited state (Fig.1).

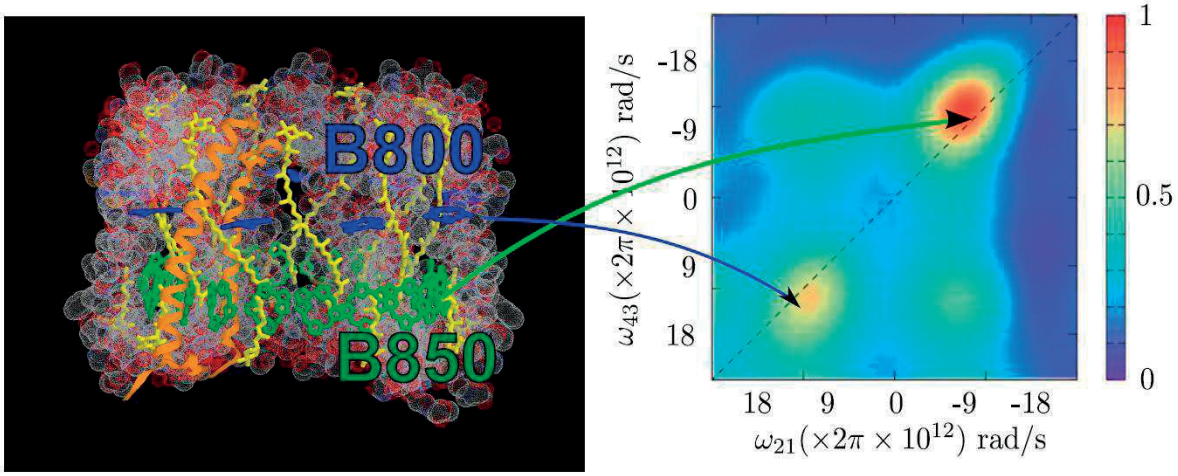

Fig.1. Left: LH2 structure. Right: Fluorescence detected 2D spectrum of LH2 at population time T = 0.

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I21

Excited by light – for forty years!

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This occasion gives me the opportunity to be a bit nostalgic, but most of my presentation will describe what I think is some of the highlights in this forty years of research.

I22

Delocalization and Electron Transfer in Conjugated Systems

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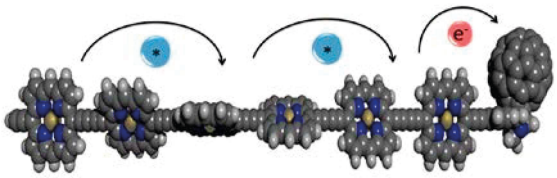
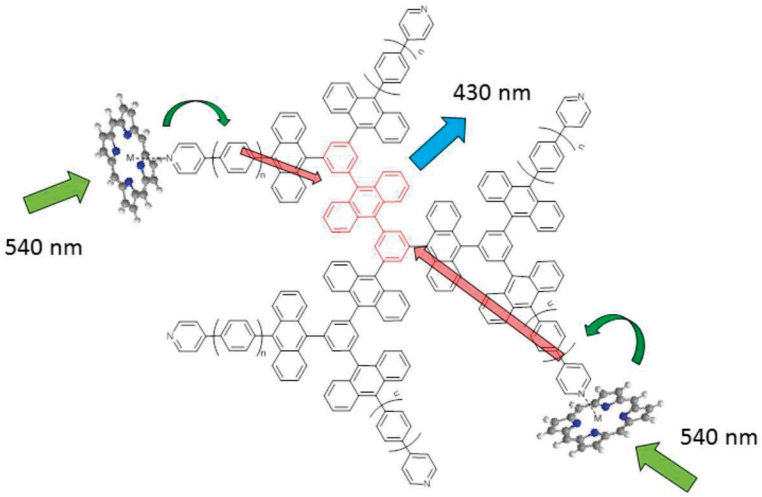
Delocalization in large conjugated organic systems has a profound influence on the performance of photo voltaic devices such as bulk heterojunction solar cells. In this talk I will discuss two systems where we have studied how the degree of delocalization governs the rate of charge separation and triplet-triplet annihilation up-conversion (TTA-UC), respectively.



In the first example, electron transfer reactions in fullerene appended porphyrin oligomers, $\mathbf{P_n\text{-}C_{60}}$, were found to depend strongly on the conformation of the porphyrin oligomer. It was shown how excitation of different conformations or restriction of oligomer conformation through chemical templating greatly affects the rates and efficiency of the charge separation. Twisted conformers of $\mathbf{P_2\text{-}C_{60}}$ showed a 4 times faster charge separation rate compared to planar conformers.[1] For longer oligomers, excitation of twisted conformers can have the opposite effect since excitation energy could localize too far away from the fullerene electron acceptor for efficient charge separation.[2]

In the second example, I will discuss how rapid triplet excitation energy migration in conjugated 9,10-diphenylanthracene (DPA) oligomers and dendrimers sustain triplet-triplet annihilation up-conversion (TTA-UC). The dendrimer is sensitized two times through triplet energy transfer from a non-covalently associated porphyrin and rapid triplet energy migration leads to efficient up-conversion without the need for diffusion.[3] It is expected that further development of this system will lead to an efficient platform for diffusion free TTA-UC in solid matrices.



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O1

Investigation of the S_1/ICT equilibrium in fucoxanthin by ultrafast pump-dump-probe and femtosecond stimulated Raman scattering spectroscopy

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Fucoxanthin (FX) is one of the most abundant carotenoids in the world due to its natural occurrence in such biomass "giants" as brown algae, seaweed and marine diatoms (*1*). The presence of carbonyl group, conjugated to the FX molecular backbone, gives rise to an intramolecular charge transfer (ICT) state. The FX S_1 and the ICT are two distinct spectral species who are generally believed to coexist in an excited state equilibrium (*1*). We have applied multi-pulse time-resolved spectroscopic methods — pump-dump-probe (PDP) and femtosecond stimulated Raman spectroscopy (FSRS) — to investigate the FX excited state photodynamics. PDP experiments show that S_1 and ICT states in FX are strongly coupled and that the interstate equilibrium is rapidly (<5 ps) reestablished after one of the interacting states is deliberately depopulated. Furthermore, the PDP experiments indicate that ICT decays to a stabilized intermediate form on the molecular ground state potential energy surface, that is thermally re-equilibrated to S_0 with a reciprocal rate of ca. 20 ps. FSRS experiments show that S_1 and ICT are two vibrationally different species. The FX S_1 possesses a vibrational structure comparable to S_1 of many other carotenoids (*2*), whereas the ICT bears a vibrational semblance to the FX S_0 (*3*). The ICT FSRS spectrum exhibits characteristic C=C vibrations at 1555 cm^{-1}, that, based on the current understanding of the FX excited state structure (*1*), may act as a coupling channel for the $S_1 \leftrightarrow$ICT equilibrium.

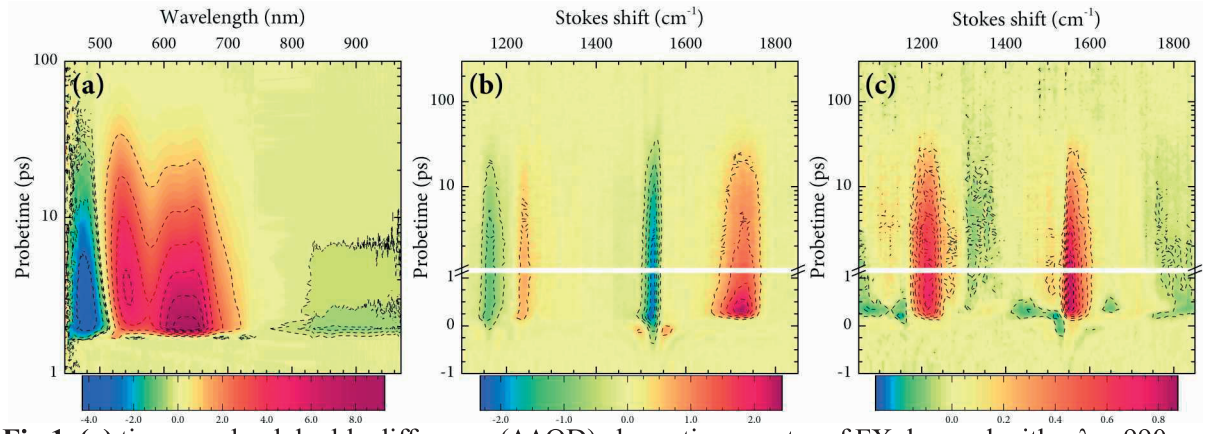

Fig.1. (a) time-resolved double difference (ΔΔOD) absorption spectra of FX dumped with a λ_D=990 nm pulse at 1.7 ps after the $S_0 \rightarrow S_2$ excitation; **(b)** FSRS spectra of the FX S_1 state (λ_{RP}=550 nm); **(c)** FSRS spectra of the FX ICT state (λ_{RP}=615 nm).

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ELECTRON TRANSFER REACTIONS IN BACTERIOPHYTOCHORME PROTEINS

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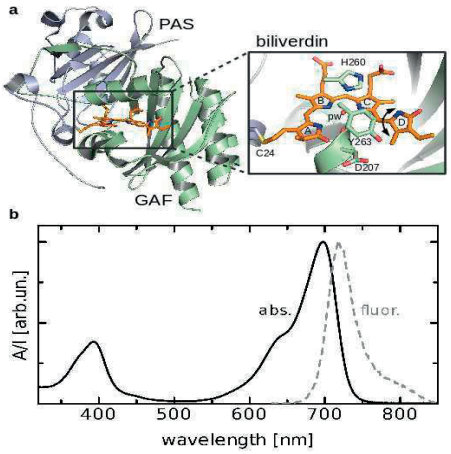

Fig. 1. Phytochrome structure and absorption properties. a*. PAS-GAF Structure of the bacteriophytochrome. Left inset: biliverdin and the C24, D207, H260, and Y263 amino acids in the vicinity b. Absorption and emission spectra of the PAS-GAF construct of Deinococcus radiodurans in its Pr state.*

Phytochromes control a multitude of reactions. It is a photoreceptor, a pigment that plants, and some bacteria and fungi, use to detect light. It is sensitive to light in the red and far-red region of the visible spectrum (Fig. 1). Phytochrome photocycle between red and far-red sensing state starts with excitation of the biliverdin molecule. The decay of the red excited state occurs through one of two competing processes: radiative, and non-radiative, including photochemisty. Up to date, non-radiative pathway of the excited states are undefined [2]. Thereby, detailed knowledge on the ultra-fast timescale photodynamics is vital for understanding the signaling mechanism of phytochromes. By utilizing ultra-fast transient absorption spectroscopy, we demonstrate the charge transfer states being central in the excited state decay processes of the phytochromes [3]. We probed experimentally in a hitherto unexplored near-infrared spectral region, providing insight about the photoinduced radical formation of the biliverdin. This study elucidates the origin of the complex excited-state decay processes and serves as a basis for the future studies of the signaling processes in phytochromes. In addition, the identified electron transfer pathway offer a new strategy in increasing fluorescence yield of bacteriophytochromes [1].

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Electron attachment to DNA bases: Potential implication in DNA damage

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Low-energy electrons have been observed to cause DNA and RNA strand cleavage even at near-zero electron kinetic energy.(*1*) This surprising result has motivated numerous studies of the cleavage mechanism; however key aspects are still not well understood. A central issue is the mechanism for electron attachment. The low-energy electrons are speculated to initially interact with the dipole moment of a nucleobase and form dipole-bound (DB) anions that possibly act as gateway states for valence bound (VB) anion formation. The excess electron is subsequently transferred from the nucleobase VB anion to the DNA backbone where cleavage can occur.(*2*) The ability of DB states to serve as electron capturer and gateway for VB states is however still not well-understood. To gain new insight into the interaction between low-energy electrons and nucleobases we have performed femtosecond time-resolved photoelectron velocity map imaging investigations on iodide-nucleobase anionic complexes of adenine, uracil, and thymine combined with quantum chemical calculations.(*3-5*)

The results presented in this contribution shows that all the investigated nucleobases can form DB anions. When energetically feasible, the DB anion can transition into a VB anion which is manifested in the data by matching decay and rise components of the DB and VB anion transients, which is most prominent in the A3 tautomer of adenine. For thymine and uracil a small fraction of the DB state decays into the VB state, while biological adenine only exhibits stable DB anions. These results represent the first direct observations of nucleobase DB anions transitioning into VB anions, and shed new light on the potential implication of nucleobase anions in DNA damage.

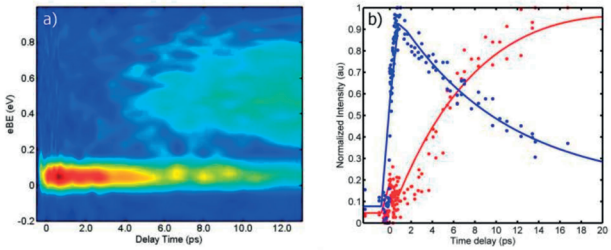

Fig.1. a) Contourplot and b) transients of I^-·Adenine

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I23

Direct, sub-picosecond tracking of structural and electronic degrees of freedom using X-ray Free Electron Lasers

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Since 2010, it has been possible to use X-ray Free Electron Lasers (XFELs) for the study of photochemical reactions on sub-picosecond timescales in solution. This talk will describe a series of recent experiments where we have investigated a range of transition metal systems of both fundamental and applied interest, from the [Pt2POP4]2+ anion to novel iron-based photosensitizer compounds. In several of the experiments simultaneous acquisition of both X-ray scattering and spectroscopic data was utilized to obtain a full-field “molecular movie” including both electronic and structural dynamics, observed in real-time as the ensemble of molecules traverses the potential energy landscapes.

O4

Near-unity Solar Energy Conversion from Iron Sensitizers

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Conversion of solar energy in photovoltaics or photocatalysis relies on the sensitization of a semiconductor or catalyst. Rare metals are typically used for this purpose due to their favorable photophysical properties, but such elements are not sustainable for large-scale production. Iron complexes has long been suggested as abundant alternatives to the widely used ruthenium compounds, but the sub-ps excited states of the iron analogues have rendered them inefficient for sensitization (1). We have recently developed a series of iron–nitrogen–heterocyclic-carbene sensitizer with excited-state lifetimes nearly a thousand-fold longer than that of traditional iron polypyridyl complexes (2-4). By a combination of transient absorption spectroscopy and transient terahertz spectroscopy we have been able to track electron injection from the iron complex into the conduction band of titanium dioxide, with a resulting quantum yield of 92%, as shown in Fig. 1 (5). These results enable the development of new solar energy-converting materials based on abundant elements.

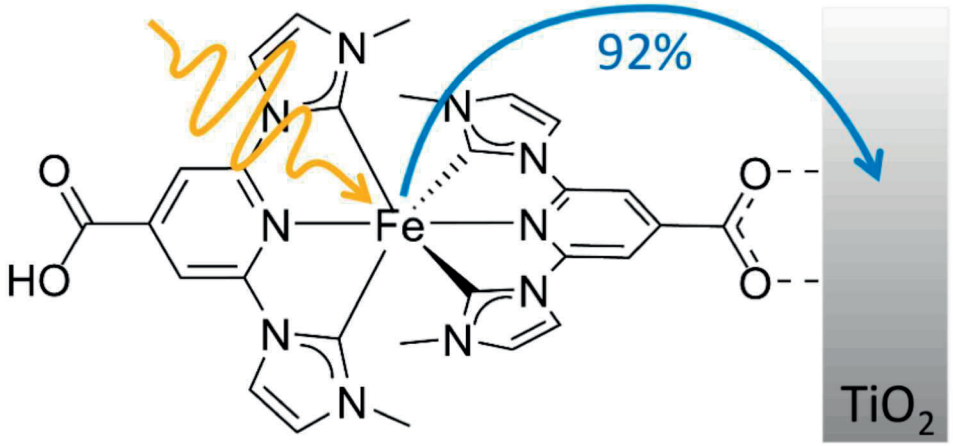

Fig.1. On of our recently developed iron complexes has an excited state lifetime three orders of magnitude longer than conventional iron-complexes. Upon illumination it injects electrons into the conduction band of TiO_2 with a quantum yield of 92 %.

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O5

Direct visualization of fundamental reaction events in solution with femtosecond time-resolved wide-angle X-ray scattering

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The earliest events in chemical reactions are critical in determining their outcome. Ultrafast spectroscopy has been instrumental in understanding chemical reactions on a sub-picosecond time scale. However, spectroscopy is indirectly sensitive to structural changes of the solute and solvent. Important questions therefore remain unanswered: What structural changes occur at the earliest moments in chemical reactions? What role do solvent dynamics play?

Femtosecond time-resolved wide angle X-ray scattering (TR-WAXS) has the ability to probe inter-atomic distances directly at the sub-picosecond timescale. We use TR-WAXS to visualize bond-scission in the photochemical dissociation of triiodide (I_3^-, see Fig. 1). Our data monitors the separation of the dissociated I atom from the parent molecule and its subsequent ejection from the solvent cage in real-time.

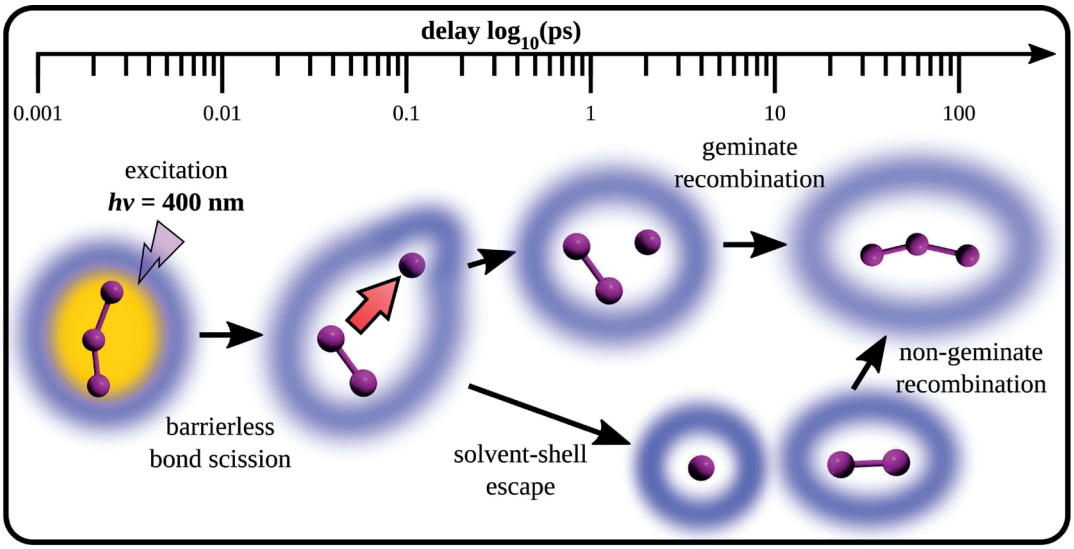

Fig. 1: Schematic representation of the light-triggered barrierless dissociation of diiodomethane referenced to an approximate time scale. Solute species are represented as ball-and-stick models, the solvent cage is represented in blue.

We will also discuss the current state of the structural modeling which aims at gaining a comprehensive description of the structural evolution of the separated species from femto- to nanosecond time scales.

O6

Femtosecond X-ray scattering study of ultrafast photoinduced structural dynamics in solvated $[Co(terpy)_2]^{2+}$

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Time-resolved X-ray scattering experiments can be used to monitor the structural changes in transition metal complexes upon light-induced excitation. Free electron lasers provide ultra-short X-rays pulses and high flux so that structural dynamics of the excited species can be recorded at the femtosecond time scale.

We have studied the structural dynamics of photoexcited $[Co(terpy)_2]^{2+}$ in aqueous solution with laser pump/X-ray probe X-ray scattering experiments conducted at the Linac Coherent Light Source (LCLS). Through direct comparisons with DFT calculations our analysis shows that the photoexcitation event leads to elongation of the Co-N bonds, followed by coherent Co-N bond length oscillations arising from impulsive excitation of a vibrational mode dominated by the symmetrical stretch of all the six Co-N bonds and having a period of 0.34 ps. This mode decays on a sub-picosecond time scale leading to a bond-elongated excited state structure associated with a high spin (HS) state that subsequently decays to the low spin (LS) ground state with a ~7 ps lifetime.

The short but exceptionally intense X-ray pulses from the LCLS combined with the so-called “timing tool” allowed a time resolution < 100 fs, such that, for the first time in solution, the ultrafast structural dynamics following LS → HS excitation of a SCO Co-compounds could be investigated.

This project was conducted as a collaboration between the following groups:
M. Nielsen, K. Møller Center for Molecular Movies Group, DTU (Denmark)
V. Sundstrøm Chemical Physics Group, Lund (Sweden)
G. Vanko Group, Budapest (Hungary)
C. Bressler FXE-group, Hamburg (Germany)
K. Gaffney Group, SLAC (USA)
XPP end station staff, LCLS (USA)

I24

Charge carrier motion in organic solar cells

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Bulk heterojunction (BHJ) architecture is currently considered as a most promising conception for fabrication of cheap and efficient organic solar cells. Photovoltaic solar cells based on organic BHJ now achieve a power conversion efficiency of >9%. In these devices, two organic materials with electron donating and accepting properties are mixed together to produce nanostructurised films with tens of nanometers domains. It is still not clearly understood how charges separate and how subsequently the free charge carriers move.
We used several optical and optoelectrical investigation methods including those with ultrafast time-resolution to address the carrier motion dynamics in bulk heterojunction and planar solar cells fabricated from polymers or "small" molecules with fullerene and its derivatives. Optical probing of the electric field dynamics by means of Stark effect and electric field-induced second harmonic generation was used to examine motion of charge carriers with subpicosecond time resolution, while conventional transient photocurrent and time delayed collection field techniques were used to address carrier motion, extraction and recombination dynamics on longer time scales.

The investigations revealed electron and hole mobility dynamics and importance of the carrier diffusion in separation of bound charge transfer states, clarified their dependences on the material morphology and roles in preventing geminate and nongeminate carrier recombination. Comparing carrier motion dynamics in samples with different stoichiometric ratios and also in planar bilayer devices we were able to distinguish between electron and hole motions and to relate them to efficiency and dynamics of dissociation. We conclude that electrons by rapidly diffusionaly moving inside sufficiently large fullerene domains move out from less mobile holes during dissociation of interfacial excitons. Therefore blend morphology enabling fast electron motion by sufficiently large distances exceeding Coulomb attraction radius enables efficient charge carrier generation.

We used the stochastic Schrödinger equation (SSE) to model the system evolution, which allowed us to investigate how the charge carrier separation process is affected by the interplay between coherent dynamics and decoherence, dephasing and relaxation effects. We analysed the carrier delocalization phenomena by rigorous mathematical treatment. We found that initially electron is transferred only to the nearest neighbour acceptor sites, then due to intermolecular interactions in the acceptor domain the electron becomes delocalized according to the principles of quantum mechanics. Consequently, the electron becomes coherently transferred to distant sites from the hole. Later the lattice relaxation causes electron self-trapping and partial localization turning coherent wave-like propagation into incoherent classical hopping.

O7

High Charge Mobility Limit in CH3NH3PbI3 Revealed by Coherent Acoustic Phonons

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Methyl ammonium lead iodide, CH3NH3PbI3, is an organic-inorganic semiconductor that has received an enormous amount of attention in recent years for its potential in solar cell technology [1, 2]. Despite the record breaking applications that have been demonstrated using this material, there is a lack of understanding of its intrinsic properties. For example, in the literature, the mobility spread out over three orders of magnitude. It is therefore critical to study the material properties in the simplest morphology of the perovskite: single crystal.

Within a crystal, mobility is limited by the intrinsic and extrinsic factors. Extrinsic factors, such as defects, are sample dependent, while intrinsic are properties of the crystal. In a perfect crystal, i.e. without any defect, mobility is limited by the scattering of electrons with acoustic phonons, the so-called deformation potential scattering. Obtaining the acoustic phonon limited mobility of carrier is thus crucial for researchers to have a target to aim at in their device preparation.

Here, we applied femtosecond time-resolved pump-probe spectroscopy to generate and detect coherent acoustic phonons. [4] The absorption of an intense laser pulse leads to the generation of excited carriers, which rapidly transfer their excess energy to the lattice, thus creating coherent acoustic phonons. We were able to extract the deformation potential of electrons and holes by relating the density of photo-excited carriers and their excess energy to the amplitude of the generated coherent acoustic phonons. We then calculate the intrinsic mobility of electrons and holes in $CH_3NH_3PbI_3$ and compare these results with recent Hall effect and THz measurements. We have obtained relatively high intrinsic charge mobilities that can serve as a target in future $CH_3NH_3PbI_3$ device preparations.

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Carrier Recombination Processes in Indium Gallium Phosphide Nanowires

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Indium Gallium Phosphide ($In_{1-x}Ga_xP$) nanowires (NWs) with bandgap tunable from 1.34 to 2.26 eV, have potential applications in solar cells, light emitting diodes and tunable NW lasers.[1,2] Understanding recombination and photoconductivity dynamics of photo-generated charge carriers in $In_{1-x}Ga_xP$ NWs is essential for their applications. It is also important to study fundamental processes related to Ga composition in $In_{1-x}Ga_xP$ NWs.

We have investigated the dynamics of photo-generated charge carriers in a series of $In_{1-x}Ga_xP$ NWs with varies Ga compositions. Time resolved photo-induced luminescence (TRPL) (Figure 1 (a)), transient absorption (TA) and time resolved THz (TRTS) (Figure 1 (b)) measurements were performed to investigate dynamics of radiative and non-radiative charge recombination and photoconductivity in these NWs. We attribute the observed decay of PL to trapping of photo-generated charges as PL decay time increases with increasing excitation density due to the trap filling effect. Trap filling effect in $In_{0.46}Ga_{0.54}P$ and $In_{0.65}Ga_{0.35}P$ NWs was also observed in TRTS measurements, which are dependent on electron mobility. From TA measurements, we conclude that non-radiative recombination of charges is much slower than radiative, consistent with the observation of long-lived photoconductivity. Dependence of TRPL and TRTS dynamics of Ga composition suggest that both electron and hole trapping becomes faster with increase of Ga in $In_{1-x}Ga_xP$ NWs. We could not observe a pronounced dependency of non-radiative recombination on Ga composition.

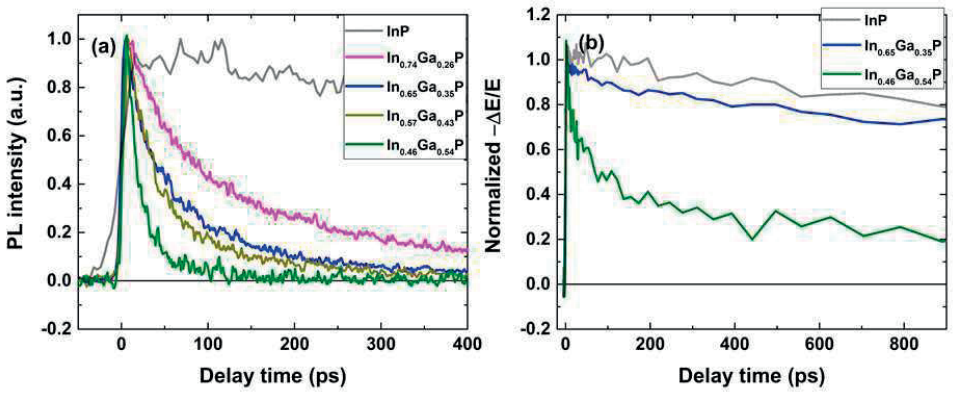

Figure 1: (a) TRPL decay of InGaP NWs with different Indium contents after photo-excitation at 400 nm (3.1 eV). (b) Normalized photoconductivity change of InP, $In_{0.65}Ga_{0.35}P$, and $In_{0.46}Ga_{0.54}P$ NWs.

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O9

Photophysical Study of a Self-Assembled Donor–Acceptor Two Layer Film on TiO_2

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The study of organic molecules at semiconductor interfaces is a key issue in the development of novel hybrid architectures with controlled charge-carrier transport pathways in organic photovoltaic and sensor devices.

In the present study, a new method for the deposition of donor–acceptor two-layer molecular films using the self-assembling approach is proposed and used to construct ordered DA architectures on a mesoporous film of TiO_2 nanoparticles [1]. The method is based on using two compounds with different lengths of linkers responsible for the layer self-assembly. First, fullerenes equipped with a short linker forms the primary SAM on TiO_2. Then, porphyrins with a long linker, which can penetrate between the units in the first monolayer, form the secondary layer on top of the fullerenes (Figure 1).

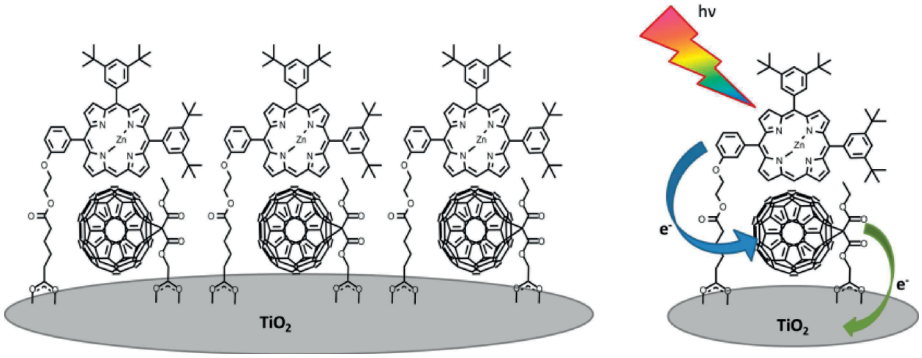

Fig.1. Donor-acceptor self-assembled two layer on TiO_2.

The photophysics of self-assembled layers at the TiO_2 interface were examined by steady-state and time-resolved transient absorption spectroscopy methods. The selective excitation of porphyrin chromophore revealed enhanced emission quenching in the presence of fullerene in bilayers and a fast (<5 ps) intermolecular electron transfer (ET) taking place from porphyrin to the fullerene layer. These confirmed the formation of the interlayer donor–acceptor interface. Furthermore, the primary charge separation between the fullerene and porphyrin layers was followed by the electron transfer from the fullerene anion to TiO_2. Importantly, due to spatial separation between the primary electron donor and TiO_2, the charge recombination process was significantly decelerated compared to single chromophore sensitized TiO_2.

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O10

Exploring the role of TiO_2 in the CO_2 reduction by Re catalyst

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Tremendous efforts have been made to explore new energy resources in order to face the energy shortage problem and the global warming problem.[1] Continuous increasing of CO_2 concentration is the main reason behind the global warming. A smart way is to convert the CO_2 to fuels or other useful chemicals, which is one of the goals of artificial photosynthesis.[2] Photo-electro catalytic reduction of CO_2 has been achieved by employing many different systems starting with p-type, n-type semiconductors and enzymes. The formers suffer from the poor selectivity and, in contrast, the later shows excellent selectivity but suffers from stability issues.[3] Achieving both high selectivity and stability can be done by using synthetic molecular catalyst for CO_2 reduction. Generally, there are two main approaches to use the synthetic molecular catalyst in CO_2 reduction. In the first approach, the catalyst receives electrons from a photosensitizer after excitation. Whereas in the second approach, the catalyst, itself, plays the dual role, working as photosensitizer and catalyst at the same time.

Rhenium tricarbonyl bipyridine bromide (***Re(bpy)(CO)$_3$Br***) catalyst can play the dual role as photosensitizer and as catalyst. Recently, Reisner's group managed to improve the CO_2 reduction using this catalyst by attaching the catalyst to n-type TiO_2 semiconductor *via* phosphonic acid (ReP-TiO_2) as linkers in the presence of triethanolamine (TEOA) as an electron donor.[3]

In the present work, we are trying to explore the role of TiO_2 in such catalytic activity improvement. By using IR transient absorption spectroscopy from fs up to sec time scales we managed to follow the electron injection from the excited catalyst (on ps time scale). On the same time scale TEOA is able to regenerate the oxidized Re to neutral Re. The singly reduced Re observed on µs to sec time scale, where the electrons still in TiO_2 conduction band, which means that the TEOA radical can reduce the neutral Re to the singly reduced Re.

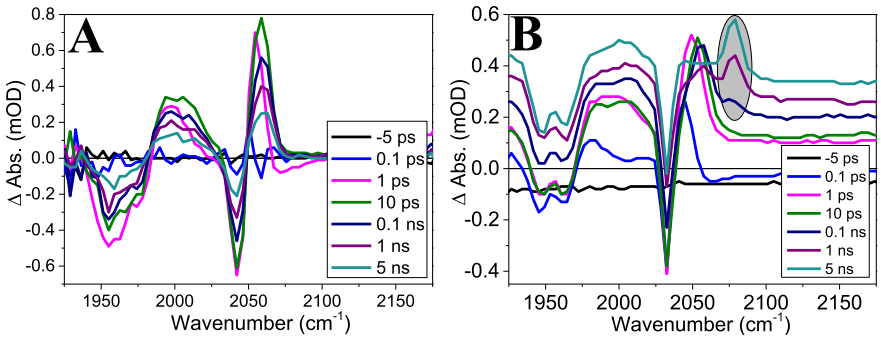

Fig. 1. ReP-ZrO_2 no electron injection (A) and ReP-TiO_2 electron injection (B).

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I25

Ultrafast Dynamics of Thiolate-Protected Gold Nanoclusters

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An important fundamental question in chemistry and nanoscience concerns the behavior of systems when their size increases from atomic limit towards bulk matter. Considering metal nanoparticles, a key property in this regard is the existence or absence of a band gap or HOMO-LUMO gap. Upon closing the energy gap, properties change from molecular-like towards metallic. We have studied this general question via ultrafast photodynamical studies of well-defined ligand-protected gold nanoclusters having 102 – 144 gold atoms. Whereas bare metal clusters are highly reactive and unstable, organic ligand-shell makes clusters stable at room temperature and in solution phase. Energy relaxation dynamics is an excellent probe for the electronic structure since it is very sensitive to the existence of an energy gap and thus dramatic difference in dynamics is expected to occur when the gap closes. The present study shows strikingly that the transition from molecular to metallic behavior occurs between ~130 and 144 gold atom clusters. By combining experimental and theoretical work, we are able to present a complete picture of relaxation dynamics for the studied clusters, showing several timescales for relaxation from subpicosecond to longer than nanosecond. Surprisingly, our study reveals an important role of the triplet state in the molecular clusters.

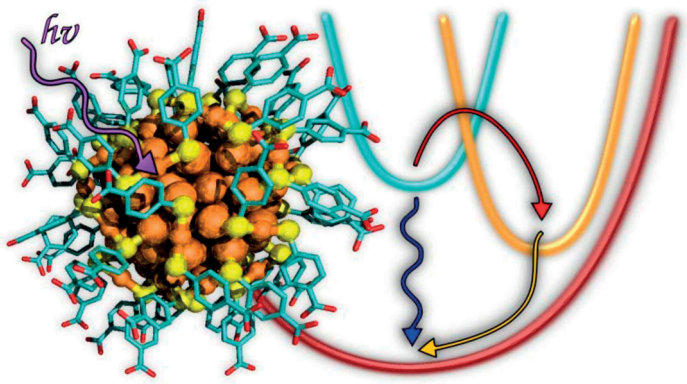

Fig.1. $Au_{102}(pMBA)_{44}$ nanocluster (pMBA = para-mercaptobenzoic acid) and schematic presentation of its lowest electronic states.

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O11

Ultrafast Dynamics in DNA Templated Silver Clusters

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DNA templated silver nanoclusters (AgNC) in the size range of a few tens of atoms or less have come into prominence over the last decade due to very favorable absorption and emission properties. Applications in microscopy and sensing are already implemented(*1*), however little is known about the excited state structure and dynamics of these clusters.
We perform detailed investigations of the energy-level structure in a 20-atom AgNC(*2, 3*) and characterize the early-time relaxation cascade which eventually results in the population of an emissive state using polarization controlled femtosecond coherent two-dimensional electronic spectroscopy (2DES). A phenomenological excited state structure is determined, and we identify an ultrafast intra-cluster transfer process which couples strongly to a vibrational mode, resulting in the transfer of both population and coherence on a sub-100 fs timescale. By drawing analogies to gold nanoclusters(*4, 5*), this transfer is interpreted as transfer from core- to shell-states coupled to cluster breathing modes.

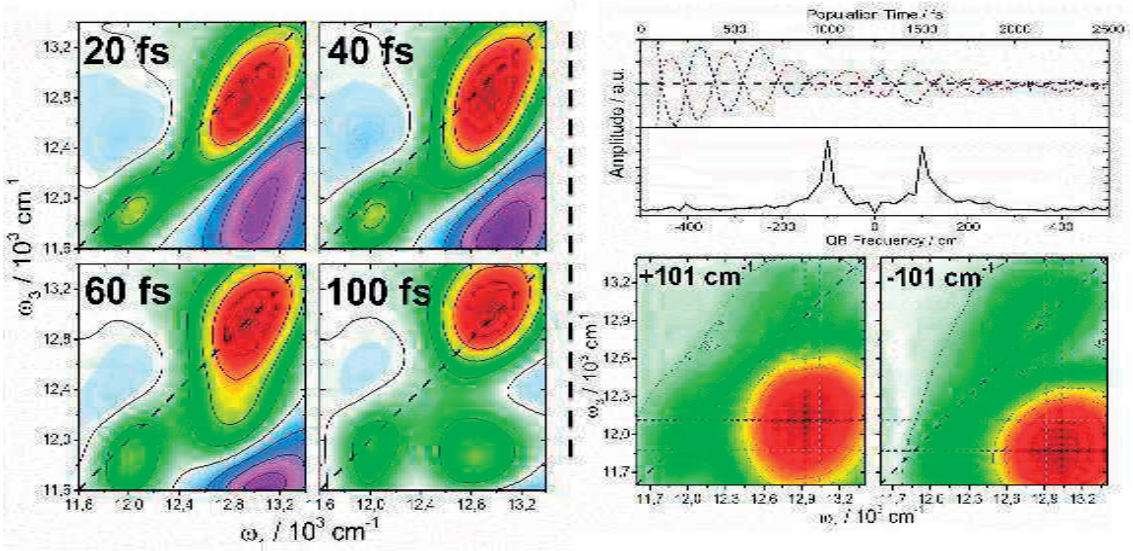

Fig.1. Left: Snapshots of the early-time relaxation at 77 K. Right: Strongly oscillating residuals, integrated Fourier transform amplitudes of quantum beats, and amplitude maps of the dominant 101 cm^{-1} quantum beat mode.

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O12

Spatiotemporal imaging of few-cycle nanoplasmonic fields using photoemission electron microscopy

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Surface plasmons can concentrate light on both a nanometre spatial and femtosecond temporal scale, and thus serve as a basis for nanotechnology at optical frequencies. However, the simultaneously small and fast nature of surface plasmons leads to new challenges for spatiotemporal characterization of the electric fields. To overcome this, we use photoemission electron microscopy (PEEM) in combination with state-of-the-art sources of ultrashort light pulses. The first approach is based on the extension of interferometric time-resolved PEEM (ITR-PEEM) *(1)* to the few-cycle regime by using two synchronized pulses from an ultra-broadband oscillator *(2)*. Because of the photon energy (1.2-2.0 eV) being well below the material work function, photoemission occurs through a multiphoton process. The measurement is performed by scanning the delay between two identical, sub-6 fs pulses and measuring the local photoelectron yield (Fig. 1). The second approach is based on using high-order harmonic generation (HHG) to produce attosecond pulses in the extreme ultraviolet (XUV) region. Attosecond XUV pulses have been proposed to enable a direct spatiotemporal measurement of nanoplasmonic fields with a temporal resolution down to 100 as *(3)*. However, PEEM imaging using HHG light sources has turned out to be a major challenge due to issues such as space charge effects, chromatic aberration, and poor image contrast *(4-6)*. To help with these issues, we perform HHG using a new optical parametric chirped pulse amplification system delivering 7 fs pulses at 200 kHz repetition rate, and show the superior performance of this light source compared to traditional low-repetition rate HHG systems.

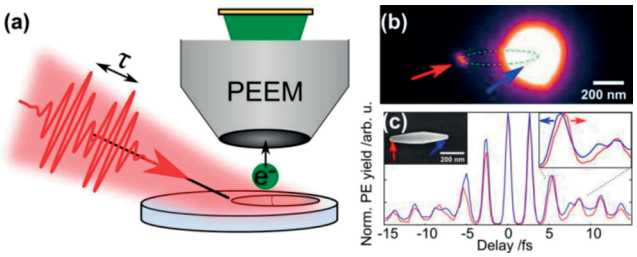

Fig. 1. (a) Schematic of an ITR-PEEM experiment. (b) Multiphoton PEEM image of an individual rice-shaped silver nanoparticle. (c) Normalized photoemission yield from the two ends as a function of delay between two identical, 5.5 fs pulses. The differences between the two curves for delays between ~4 and ~10 fs correspond to locally different near-field dynamics during the few cycles of maximum amplitude. Figure adapted from ref. *(2)*.

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O13

Tracking vibration of a molecule - Time-resolved single molecule spectroscopy using nanoantennas

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Utilizing plasmonic nanostructures as optical antennas is a convenient way to amplify signals from nearby molecules. The intensity enhancement by nanostructures has been successfully exploited in many *single-molecule surface-enhanced Raman scattering* (SM-SERS) studies (*1*). Necessary conditions for single molecule detection, typical signatures of individual molecules, and mechanisms of SERS enhancement by nanoparticles are now relatively well understood. The surface enhancement schemes for detecting individual molecules have been recently extended to nonlinear four-wave mixing techniques, namely *coherent anti-Stokes Raman scattering* (CARS) (*2*). The technique holds promise for even greater sensitivity than regular SERS. This is due to the intensity scaling of the surface-enhanced version of CARS to the eight power of the enhanced local electric fields created by the three-pulse excitation. Despite the rapid developments in the SM-field, spectroscopic studies of individual molecules with a femtosecond time-resolution have been largely unexplored.

In this presentation I will discuss our recent experimental demonstration of capturing vibrational motion of a *single* bipyridyl ethylene (BPE) molecule with a fs time-resolution (*3*). In the experiment, coherent evolution of vibrational superposition in a single molecule was tracked for 10 ps using a femtosecond CARS technique. The evolution of the molecular coherence was followed inside a single plasmonic nanoantenna amplifying the CARS intensity. Antennas used in this work were engineered by combining colloidal gold nanoparticles (diameter ~ 90 nm) inside a silica casing with the BPE reporter. I will highlight the unique CARS time traces observed from individual molecules, and contrast them with the ensemble measurements of BPE. I will show how the time traces inherently carry the information of the number of molecules producing them, and demonstrate how this relates to the theoretical framework of CARS. I will also briefly discuss some of the properties of antennas themselves, such as elastic scattering and SERS (4).

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I26

Ultrafast conductivity dynamics of electrons in glasses and water

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The free electron plays a crucial role in chemistry and solid state physics, for instance in chemical reactions in the aqueous phase and as charge carrier in photovoltaic systems. Whereas the behaviour of electrons in such systems in general are well understood down to the femtosecond time scale, the conductivity of the electron in disordered systems such as amorphous solids and liquids is difficult to describe theoretically, and is subject to considerable experimental interest. The conductivity is directly related to the degree of localization and thus the mobility of the electron. Experimental determination of the conductivity spectrum gives direct information about the scattering time and mean free path of the electron, as well as information about trapping dynamics in a disordered environment.

Here we report on time-resolved terahertz (THz) spectroscopy (TRTS) of photoinjected charge carriers in chalcogenide glass and water. The nonresonant nature of conductivity processes results in a broadband response. We use ultrabroadband THz spectroscopy based on THz generation in femtosecond two-color air plasma and air-biased coherent detection of the field, as illustrated in Fig. 1(a). Figure 1(b) shows the photoinduced conductivity spectrum of electrons in a chalcogenide glass, where the fitted curves offer values for scattering time, confinement degree and carrier concentration.

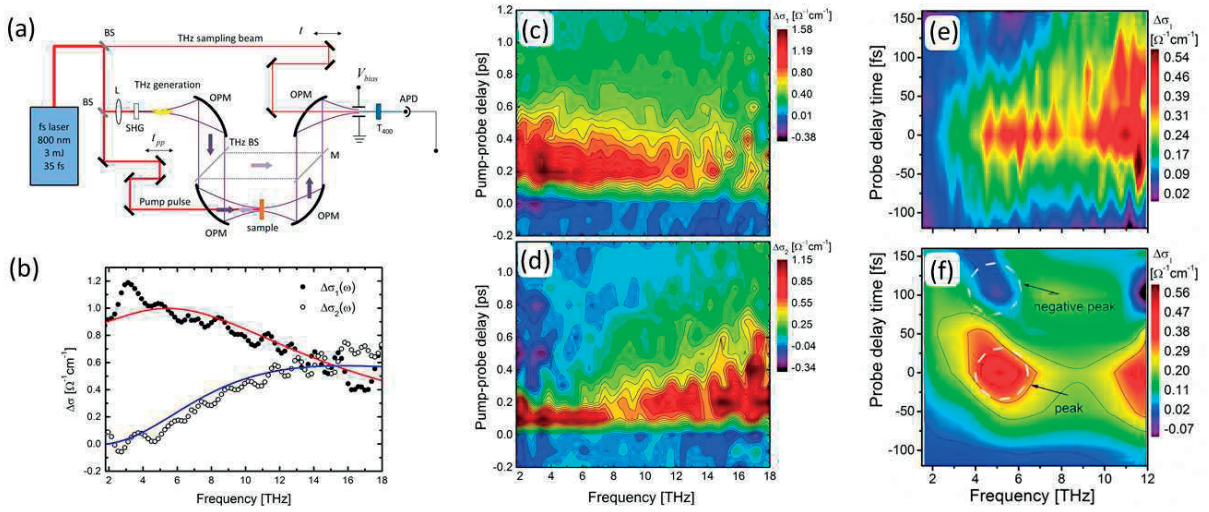

Fig.1. Time-resolved THz spectroscopy (a) of the conductivity of photoinjected electrons in a chalcogenide glass (b-d) and water (e-f).

The photoconductivity of disordered materials evolve on a femtosecond time scale, as seen in Fig. 1(c-d) for the chalcogenide glass and for photoinjected electrons in water (e: experiment; f: simulation). As will be discussed, we show that the photoinjected electron in water is subject to an ultrafast 18-fold increase of its effective mass during the initial solvation process.

O14

Ultrafast excited-state intramolecular proton transfer in symmetric doubly hydrogen-bonded Schiff bases

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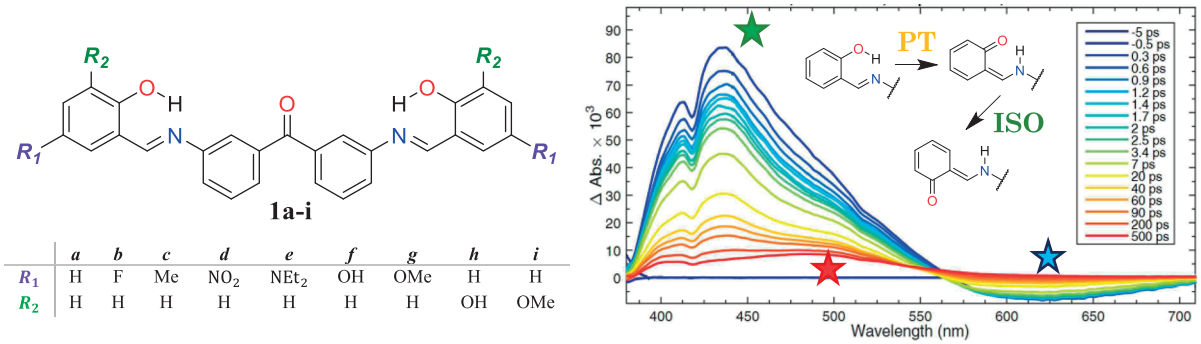
Recent progress in the study of ultrafast excited-state intramolecular proton transfer (ESIPT) reactions has illustrated the effect of the geometry (*1*), and the substituent together with the solvent (*2*) on model systems in which a single proton transfer can take place. Aiming towards a deeper understanding of electronic substituent effects, we studied a series of symmetrically substituted Schiff bases with the potential for double proton transfer reactions (**Fig. 1**) through fs transient FTIR and UV-Vis techniques, with (TD)-DFT calculations used to guide the understanding of the system.



	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
R_1	H	F	Me	NO_2	NEt_2	OH	OMe	H	H
R_2	H	H	H	H	H	H	H	OH	OMe

Fig. 1: Compounds studied in this work (*left*) and typical transient absorption spectra for compound **1a** in a polystyrene film (*right*): fluorescence of the *cis*-keto tautomer (★), $Z \rightarrow E$ isomerisation of the excited keto tautomer (★), and long-lived ground-state *trans*-keto photoproduct absorption (★).

All compounds exhibit ultrafast ESIPT (<200 fs) that is not slowed down significantly by either solvent or temperature. The corresponding *cis*-keto tautomers isomerise within ca. 15 ps to the *trans*-keto form probably through a conical intersection. Interestingly, these compounds also exhibit solid-state fluorescence and photochromism, with a photoproduct mean lifetime of ca. 2 h in a rigid matrix and ca. 250 µs in acetonitrile solution. The drastic increase in lifetime on the rigid matrix strongly suggests that the photoproduct is, in fact, a *trans*-keto form that thermally reverts to the *cis*-enol form. Intersystem crossing is ruled out by nanosecond flash photolysis experiments carried out under both Ar and O_2 atmospheres, where no changes were observed in the kinetics of the long-lived component (corresponding to the ground-state *trans*-keto absorption). One still unanswered question is whether one or two protons are transferred, with computational studies strongly suggesting the excited-state transfer of a single proton.

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O15

Cobalt-porphyrin for water oxidation on FTO surface, molecular or metal oxide catalyst?

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Water splitting has long been perceived as the Holy Grail to produce a green and renewable fuel. This process can be divided in two chemical reactions: water oxidation and proton reduction. During the past years, several molecular catalysts have been synthesized in order to decrease the energy required to perform those reactions.(*1*) Recently, scientific concerns have grown to know whereas those catalysts are really molecular or if their metal oxide decompositions are acting as real catalyst.(*2*) We report, here, an investigation on a well-known cobalt porphyrin molecular catalysts for water oxidation (CoTPP for instance, TPP: 5,10,15,20-Tetraphenylporphyrin).(*3*) We manage to prove by the use of several spectroscopy techniques (such as SEM, EDS, Hard and Soft XPS) that the activity toward water oxidation was not provided by the molecular catalyst but by an ultra-thin layer of cobalt oxide provided by the decomposition of the Cobalt porphyrin.

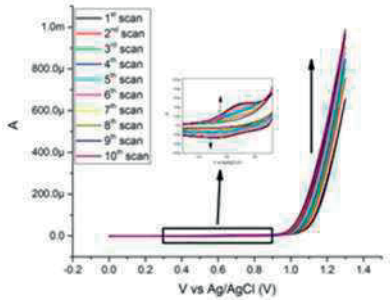

Fig.1. Cyclic Voltammetry scans of CoTPP on FTO glasses in pH9.2 solution

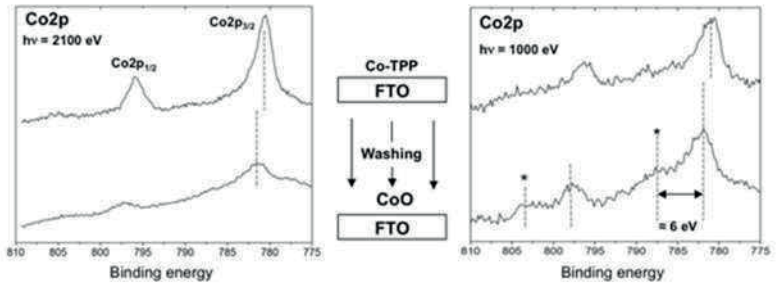

Fig.2. Detection by soft and hard XPS of the presence of CoOx on the surface of the FTO after water oxidation reaction

Further investigations of this ultra thin film reveal an extremenly high activity toward water oxidation as well as high transparency. Therefore, this new material present very interresting caracteristics for PEC cell incorporation. Moreover this work highlight the tecnical difficulty of the detection of thin layer metal oxides.

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Nature of large amplitude blinking in methylammonium lead iodide perovskites revealed by temporally and spatially resolved photoluminescence.

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Over the past few years there has been a growing interest in methylammonium lead iodide ($MAPbI_3$) perovskites as a good material for solar cells due to its broad absorption and long-lived free charges that currently yield power conversion efficiencies over ~20 % *(1)*. Despite charges being long-lived, the end result is ultimately affected by a number of non-radiative pathways present in the material associated with defects. These can be ionic vacancies, interstitials or even lattice dislocations/boundaries, but irrespective of the nature of the defect, they all inhibit the overall ability of the material to serve as a good solar cell.

In this work we applied our method called Super-resolution Luminescence Micro-Spectroscopy (SuperLuMS) *(2)* where we study photoluminescence (PL) transients and PL lifetime in local structures less than 1 um in size and correlate those results with structural properties measured with electron microscopy. Using 1 Sun (0.1 W/cm^2) excitation power we mimicked solar cell operational conditions and observed large amplitude PL blinking (Figure 1a) in correlation with spatial fluctuations of the emission profile (Figure 1b) *(3)*. Such shifts indicate that a significant part of the crystal actually goes dark. By correlating the spatial shifts with electron microscopy images we were able to determine which type of structures blink (Figure 1c). Correlating PL lifetime with blinking showed that as PL blinks down lifetime is reduced by roughly the same fraction (Figures 1 e-f). This indicates that a large part of charges suddenly find a quicker way to relax non-radiatively instead of radiatively.

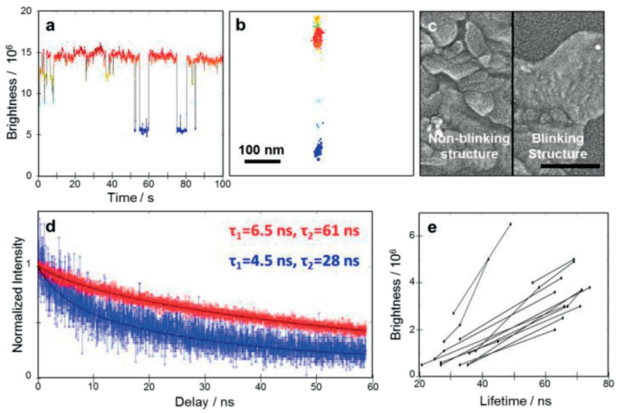

Figure 1. (a) Intensity transient in units of brightness (photons cm^{-2} s^{-1}) where two blinking events are recorded. (b) Mean positions of the emission profile in each frame showing two well-separated clusters belonging to each intensity level according to the color-coordination in (a). (c) Two regions of a polycrystals taken with SEM showing non-blinking and blinking related structures. (d) Lifetime integrated over the two intensity levels (same color-coordination). The two traces reveal a significant decrease of the slow component as intensity blinks down. (e) Statistics of 18 polycrystals where blinking amplitude and lifetime changes are recorded revealing that shorter lifetimes are measured when intensity blinks down. The dots connected with lines belong to the same $MAPbI_3$ polycrystal showing that a blinking down event always comes with a reduced lifetime.

Typically, blinking in $MAPbI_3$ nanocrystals is attributed to Auger recombination at higher excitation powers *(4)*. However, using the Stern-Volmer relation together with our observations, we show that large amplitude blinking must be the result of a single photogenerated quencher able to trap excitations at a much higher efficiency than the defects already present in the material. Such a 'super' quencher is therefore detrimental to solar cell operations.

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O17

Coherent Two-Dimensional Spectroscopy of a Fano System

Felipe Poulsen, Daniel Finkelstein-Shapiro, Tonu Pullerits, Thorsten Hansen

The Fano profile arises from a model describing the interaction of a discrete excited state and a continuum of excited states. Both set of states are reachable by photoexcitation so that the population in the continuum is the sum of two pathways - one direct and one indirect passing via the discrete state - that can interfere constructively or destructively and lead to an asymmetric resonance profile. The model has been successful in describing atomic physics spectra and more recently in nanostructured devices where relaxation and dephasing are important. The prospect of analyzing nanostructured, dissipative Fano systems with 2D spectroscopy opens the door to understanding in detail the dissipative processes that occur in a continuum. To this end we present the closed-form solution of the 2D lineshape of a Fano model in the wideband approximation and coupled to a Markovian path. We discuss the different contributions from each of the Feynman pathways and outline the physical parameters that one can measure.

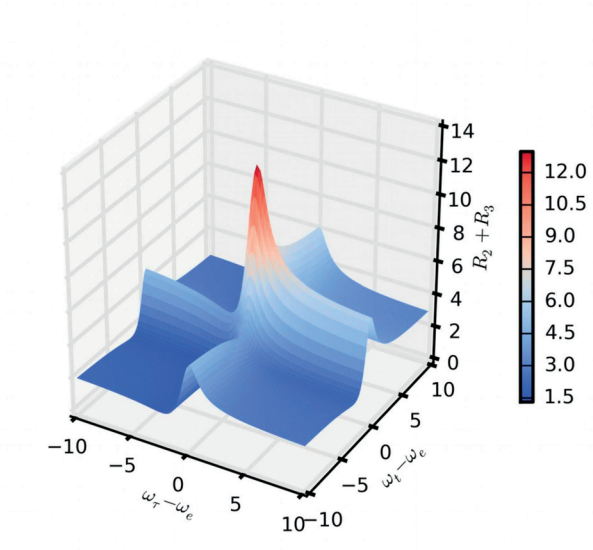

Figure 1. Absolute value of the rephasing signal of a Fano model.

O18

Detection of kinetics type from action signals of phase modulated light fields.

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Intensity-modulation of continuous laser beams have been commonly used in the life-time measuring of various action signals. The intensity modulation technique can be implemented with pulsed lasers, wherein the peak intensity of a train of pulses are modulated. An advantage of pulsed excitation is that they can induce nonlinear interactions with the media. In the discussed experimental set up, two beams with differently modulated phases are used to excite the two-photon fluorescence from a fluorophore or photocurrent in a semiconductor device. The non-linear interaction with the media splits the signal onto several ones arising from various field-matter interaction path-ways. In an ideal two-level system (linear uniform decay kinetics with short life-time of the excited state) the ratio of the primary signal to the secondary one follows the law 4:1. As we will demonstrate in the talk, deviations from this ratio, as well as generation of tertiary, quaternary and other signals is a consequence of finite-life time and/or non-linear type of kinetics in the sample. Detection of such effects is helpful not only for the life-time measuring, but also allows to determine the type of kinetics in the media.

In the talk we are going to discuss a number of models, including two-level molecular system with a finite life-time of the excited state and the model of carrier-carrier recombination in semiconductor, as well we demonstrate an analytical method for their investigation. Analysis of this models allows to set one-to-one correspondence for the type of kinetics and the observed particularities of the signals. Also, we will present experimental verification of our findings.

O19

Controlling the Photoexcited Decay of Fe(II)-*N*-Heterocyclic Carbene Complexes Through Structural Modifications

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Understanding, and subsequently being able to manipulate, the excited state decay pathways of functional transition metal complexes is of utmost importance in order to solve grand challenges in solar energy conversion and data storage. Herein we perform spin-vibronic quantum wavepacket dynamics simulations[1,2] on two functional Fe-*N*-heterocyclic carbene (NHC) complexes: the first discovered Fe(II)-NHC photosensitizer, $[Fe(bmip)_2]^{2+}$ (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)pyridine),[3] and its 3-*tert*-butyl (*t*-Bu) functionalized derivative, $[Fe(btbip)_2]^{2+}$ (btbip = 2,6-bis(3-*tert*-butyl-imidazole-1-ylidene)pyridine).[3] The results demonstrate that relatively minor variations in the molecular structure lead to completely different excited state relaxation of the initially excited singlet metal-to-ligand charge transfer (^{1}MLCT) state. In $[Fe(bmip)_2]^{2+}$, the ultrafast ^{1}MLCT→^{3}MLCT intersystem crossing is followed by a rather slow ^{3}MLCT→^{3}MC (MC = metal-centred) decay, resulting in a relatively long (5 ps) simulated ^{3}MLCT state lifetime (Fig.1a), in good agreement with the experimental 9 ps value. On the other hand, in the case of $[Fe(btbip)_2]^{2+}$, the initially photoexcited ^{1,3}MLCT state relaxes to MC states on the subpicosecond timescale (Fig.1b). This occurs because the *t*-Bu functionalization stabilizes the ^{1}MC states, enabling the ^{1,3}MLCT→^{1}MC population transfer to occur close to the Franck-Condon geometry, making the conversion very efficient. These simulations,[1,2] along-side with the time-resolved experiments,[3] demonstrate how the excited state relaxation of these Fe(II)-NHC complexes can be controlled by relatively minor changes in the ligand sphere, thus, paving the way for the design of high-efficiency transition metal-based functional molecules.

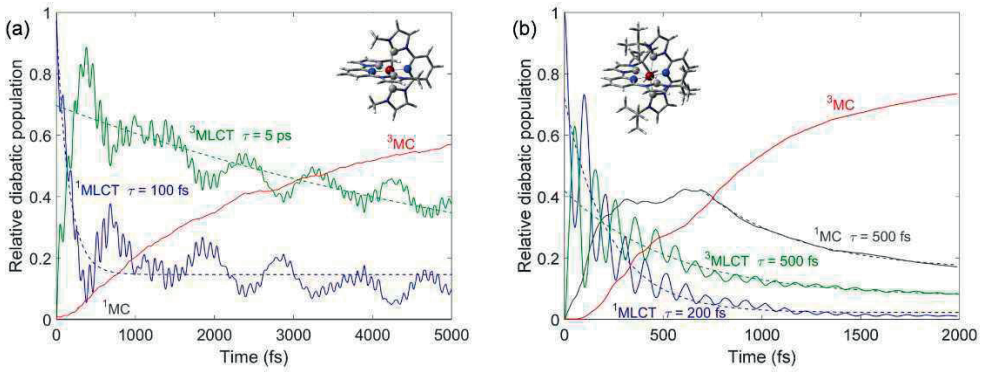

Fig.1. Population kinetics of (a) $[Fe(bmip)_2]^{2+}$ and (b) $[Fe(btbip)_2]^{2+}$ obtained from the quantum dynamics simulations.

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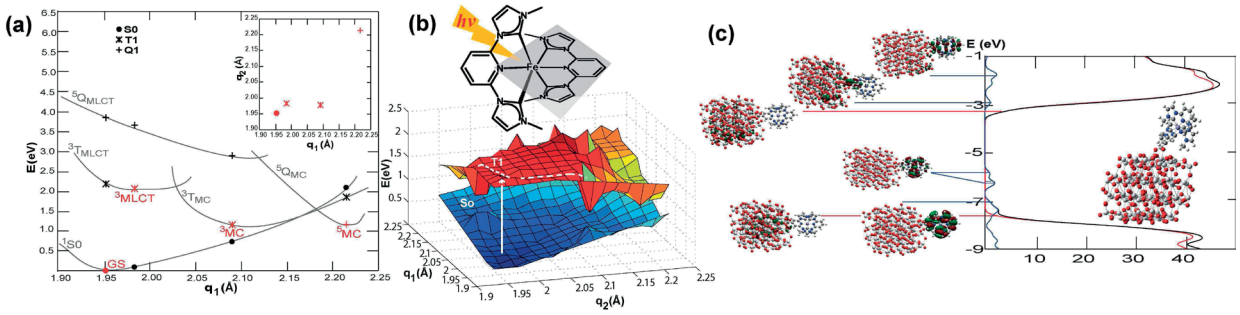
O20

Untangling Light Induced Decay Pathways of Iron-Carbenes using Theory

The viability of transition metal photosensitizers in a myriad of applications (e.g., photodynamic therapy, molecular electronics, sensitization of semiconductors, artificial photosynthesis, environmental remediation) hinges on a high-energy excited state that is sufficiently long-lived to facilitate the desirable electron-/energy-transfer process or photochemical reaction. Recent advances in ultrafast time-resolved X-ray spectroscopy provide the experimental handles to examine the structure of transient excited states, however the experimental spectra often overlap and computationally optimized excited state structures are critical to identify spectral signatures and allow for discussions of how individual excited states contribute to the overall dynamics.

Here, investigations excited state effects beyond the Franck–Condon region for earth-abdunant iron-N-heterocyclic carbene complexes that have recently exhibited remarkable 100-fold increases in excited state lifetime are used to untangle the spectroscopically observed activated decay pathways after the initial photexcitation. Unrestricted density functional theory (uDFT) optimizations of relevant minima, construction of projected potential energy surfaces, as well as multidimentional uDFT and time dependent (TD) DFT calculated potential energy surfaces are used to understand the lifetimes and dynamics of a range of homoleptic, heteroleptic, bistridentate, and trisbidentate Fe(II)-complexes.



Calculated projected potential energy surfaces (a) and multidimentional surfaces (b) of an Fe(II)-N-heterocyclic carbene and the projected potential energy surfaces of the same carbene attached to a TiO_2 nanoparticle (c).

Poster presentations

P1

Properties of static fluctuations in photosynthetic aggregates

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Static fluctuations of excitonic Hamiltonian in Frenkel exciton model in spectroscopy simulations are usually restricted to spatially uncorrelated Gaussian fluctuations of site energies. We show that the model is not sufficient to describe low temperature hole burning spectra of bacterial reaction centres [1]. Modelling results suggest that charge separation reduces energy fluctuations of specific pigments. Formally this signifies that energy fluctuations in a single exciton block and in double-exciton block must be non-trivially correlated. These correlations cannot be explained by simple tight-binding model and require introducing correlated shifts of bi-exciton binding energies.

We have shown that two-dimensional electronic spectroscopy at low temperature reveals complex interaction patterns related to the specific electronic transitions and vibrational modes [2]. Simulations of difference absorption and 2DES of photosynthetic complexes WSCP and bRC demonstrate that intermolecular correlations of site energy fluctuations can be unambiguously determined from the spectra at low temperature (Fig.1).

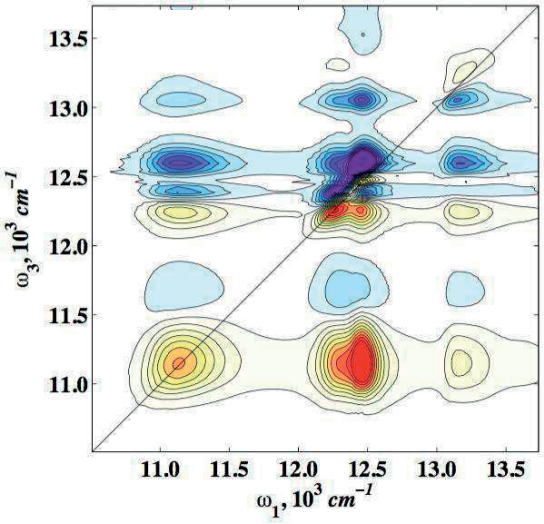

Fig.1. Two-dimensional electronic spectrum of bacterial reaction center at 5 K temperature at long waiting time.

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Redox equilibrium in Photosystem II and Tyrozine D

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The mechanism of tyrosine D (Tyr_D) oxidation in photosystem II (PSII) was investigated by EPR spectroscopy, flash-induced fluorescence decay and thermoluminescence measurements in PSII enriched membranes (BBY particles) from spinach. PSII membranes were chemically treated to reduce Tyr_D with 3 mM ascorbate and 1 mM diaminodurene and subsequent washing, leading to the complete reduction of Tyr_D. Illumination of the samples at room temperature resulted in the oxidation of Tyr_D to the same level as it was before the treatment. We have studied oxidation of Tyr_D after single flash in the absence and presence of the inhibitor DCMU (inhibitor of the Q_B site) in the pH range of 4.7-8.5. The results obtained from the fluorescence and thermoluminescence measurements show that during Tyr_D oxidation, when forward electron transport is blocked in the presence of DCMU, the $S_2Q_A^-$ recombination is absent in 10-40 % of the PSII centers (depends on pH). The Tyr_D oxidation kinetics, measured by the time resolved EPR spectroscopy was also pH dependent. At low pH values the oxidation kinetics were biphasic with a fast and slow phase, while at pH above 7.5 it was monophasic (1). In the presence of DCMU, Tyr_D oxidation kinetics was monophasic in the entire pH range, i.e. the slow phase was not observed. Based on these data and structural information we assign the fast and slow oxidation kinetics to deprotonation and water movement events in the Tyr_D vicinity.

Beyond Harmonic Oscillators: Theoretical Modelling

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Nuclear vibrations determine absorption lineshapes and may also play an important role in excitation energy transport. Vibrational models rarely go beyond the widely used harmonic oscillator model, even though realistic molecules have some degree of anharmonicity. This is also the case for light-harvesting system 2. Using a perturbation method, the eigenenergies of an arbitrary anharmonic oscillator can be found and the eigenfunctions can be written as linear combinations of the harmonic oscillator eigenfunctions. This enables the calculation of the line shape function in two ways: by computing the vibrational overlaps and by performing the cumulant expansion of the electronic gap function. This brings a new level of detail to theoretical spectroscopy and will map out the range of applicability for both the harmonic oscillator model and the morse oscillator model.

P4

Synthesis, crystal structure, photophysical and non-linear optical studies of Rhodamine 590 acid phthalate

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Potassium acid phthalate (KAP) crystals belonging to the acid phthalate family exhibit good piezoelectric, pyroelectric and electro-optical properties. They are also well known for their usage in X-ray monochromators and analyzers. The rich NLO activity arises from the influence of electron clouds of the pi bonds and also from the hyperpolarizability of hydrogen bonds. Such NLO crystals doped with luminescent laser dyes can combine its NLO property with the broadband tunability of an organic dye [1-3]. Recent studies on organic dye-doped potassium acid phthalate single crystals shows that dye-doped KAP crystals possess higher hardness, better optical quality and also rich NLO activity [4].

Hence, in this work we have presented a new co-crystal which has resulted from the inclusion of organic dye Rhodamine 590 chloride (at high concentration) into the potassium acid phthalate crystal lattice. The new NLO crystal, Rhodamine 590 acid phthalate, has been obtained from the growth solution that contains Rhodamine 590 chloride and KAP in 1:1 ratio. The obtained NLO crystals has been observed to be intensely red coloured. To explore the possibility of NLO applications of the new Rhodamine 590 acid phthalate crystal, we have computed its first-order hyperpolarizability by performing quantum chemical computations.

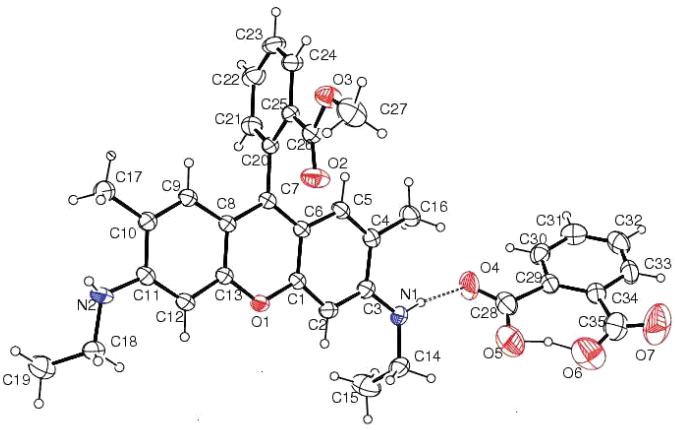

Fig 1. ORTEP diagram of Rhodamine 590 acid phthalate crystal. Hydrogen bond between the dye cation and the hydrogen phthalate anion is shown by dotted line

DFT calculations on the title compound using the widely used B3LYP functional and Pople's split-valence basis set 6-31+G* which includes polarization and diffuse functions on the main group elements as implemented in the Gaussian 03 software have been performed [5]. We have started from the crystal structure and the molecular and electronic structure of the 1:1 complex has been examined by complete structural optimization in the gas phase. Clearly, both the experiment and theory reveal that the Rhodamine 590 dye cation is bound with the

hydrogen phthalate anion through hydrogen bonding interaction H1...O4 and not through any π conjugation or covalent bonding. The structural parameters predicted by the gas phase structure of the two components in the complex show good agreement with the crystal structure given by Single crystal XRD measurements. However notable changes have been observed in the relative orientation of the components in the complex. Thus there are differences between the XRD and B3LYP/6-31+G* structural parameters in the region wherein the hydrogen bonding interaction occurs.

The total first order hyperpolarizability β_{tot} predicted for the new NLO single crystal at B3LYP/6-31+G* level is 35.27 x 10^{-30} esu. This value is 69 times higher than the first order hyperpolarizability of urea at the same level of the theory (0.51 x 10^{-30} esu). Thus the present analysis shows that the title compound can be a good candidate for NLO applications. Linear optical studies on the title compound has been carried out. Non-linear optical studies such as two-photon absorption (TPA) and two-photon excited fluorescence (TPF) on the new NLO crystal has also been recorded.

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P5

Influence of order and disorder on some photovoltaic properties of p-anthraceneethynylene-p-phenylene-vinylene copolymers - a DFT study

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Recently, the copolymer poly(p-anthraceneethynylene-alt-poly(p-phenylenevinylene) (Fig. 1) has turned out to be a promising model for the effect of order and disorder in polymer-based solar cells. By substituting alternatively linear octyl or branched 2-ethyl-hexyl sidechains to the conjugated backbone, the polymer structure can be tuned from order to disorder (*1*).

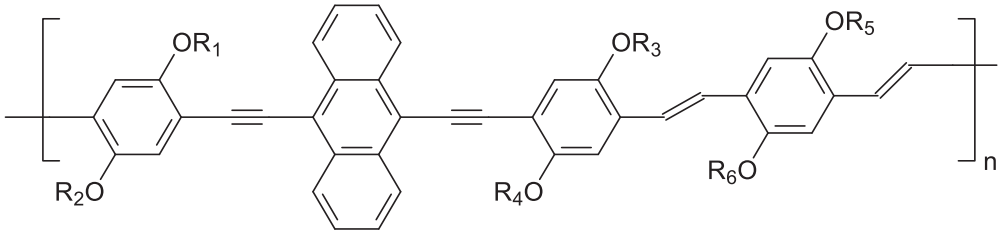

Fig.1. Chemical structure of poly(p-anthraceneethynylene-alt-poly(p-phenylenevinylene). The various substitution sites for either octyl or 2-ethyl-hexyl sidechains are assigned from R_1 to R_6.

Using Grimme's correction for dispersion in our DFT calculations, we will show that the van-der-Waals interaction between the sidechains influences the planarity of the conjugated backbones significantly. Surprisingly, we found only little order-dependent shifts in the respective absorption spectra, what is in contradiction to the experimental data (*1*). Thus the sidechain substitution mainly affects the absorption and emission spectra by the stacking of AnE-PV copolymer chains, which is only possible in semi-crystalline aggregates. Notably, this stacking is crucial for the efficiency of polymer solar cells not only in respect of optical properties but also for charge carrier separation and transport.

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Photoinduced charge carrier dynamics of Zn-Porphyrin DSSCs – the key role of charge recombination for solar cell performance

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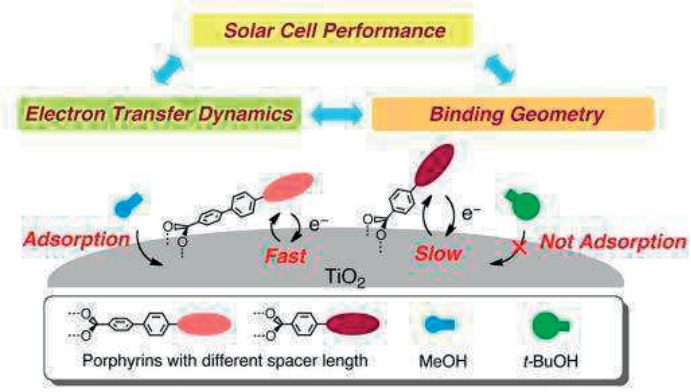
Femtosecond time-resolved spectroscopy has been used to study photoinduced electron injection and charge recombination in Zn-porphyrin sensitized nanostructured TiO_2 films. The electron transfer dynamics is correlated to the performance of dye sensitized solar cells based on the same TiO_2 electrodes. We find that the dye-semiconductor binding can be described with a heterogeneous geometry where the Zn-porphyrin molecules are attached to the TiO_2 surface with a distribution of tilt angles. The binding angle determines the porphyrin-semiconductor electron transfer distance while charge transfer occurs through space, rather than through the bridge connecting the porphyrin dye to the surface. For short sensitization times (1 hour), there is a direct correlation between solar cell efficiency and amplitude of the kinetic component due to long-lived conduction band electrons, once variations in light harvesting (surface coverage) have been taken into account. On the other hand, the long sensitization time (12 hours) results in decreased solar cell efficiency while the efficiency of electron injection is decreased.



Synthesis and Characterization of Monolayer Nickel-Vanadium Double Hydroxide for Efficient Electrochemical Water Oxidation

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Highly active and low-cost electrocatalysts for water oxidation are urgently desired due to the demands on sustainable solar fuels, while developing highly efficient catalyst to meet the industrial requirement is still challenging. Herein, we synthesized monolayer of nickel-vanadium layered double hydroxides (Ni_xV_{1-x}-LDHs). The optimized composition $Ni_{0.75}V_{0.25}$-LDH shows a current density of 27 mA cm^{-2} (57 mA cm^{-2} after ohmic-drop corection) at overpotential 350 mV for water oxidation as shown in Fig.1. To the best of our knowledge, it does not only outperform most of the well reported nickel-iron LDHs, but is also, more advanced than the other reported LDHs for water oxidation in alkaline media[1-4]. Mechanism study indicates that the nickel-vanadium LDHs can lead to higher intrinsic catalytic activity, mainly due to the better conductivity, facile electron transfer and more active sites. This work exhibits a very promising vanadium involved LDH with highly catalytic activity, and expands the scope of cost-effective electrocatalysts for water splitting.

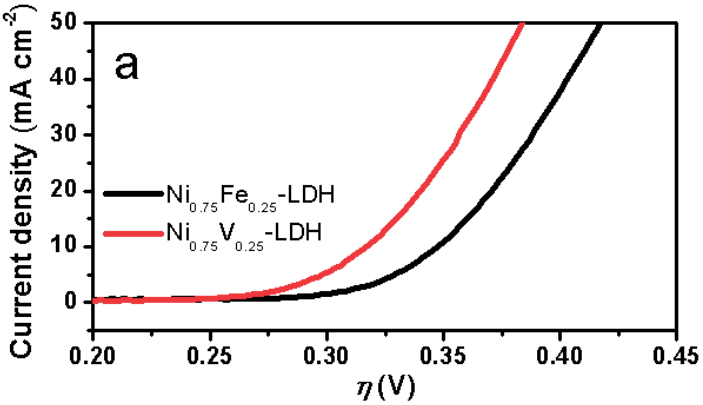

Fig.1. LSV curves of the optimized composition materials.

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Surface Plasmon Enhanced Two-Photon Absorption: Strong Emission With Fast Decay

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Metal nano-particle enhanced two-photon excitation luminescence of photosensitizers is both fundamentally important and appealing for applications, such as bio-imaging and photodynamic therapy. Quantum dots (QDs) have properties, such as high extinction coefficient, tunability of band gap via the nanocrystal size and high photo-luminescence (PL) quantum yield, which make them interesting as photosensitizers. The gold nanorod (AuNR) is a well-studied material with the localized surface plasmon resonance tunable in a broad spectral range. Therefore it is an excellent candidate for investigation of surface plasmon enhanced two-photon excitation luminescence of photosensitizers.

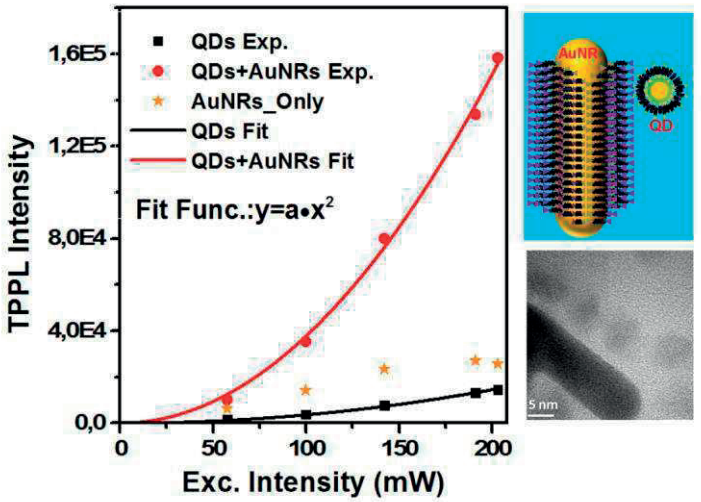

Fig.1. (a) Excitation intensity dependence of two-photon excitation photo-luminescence; (b) Schematic illustration of the QDs and AuNRs self-assembly; (c) TEM image of QD decorated AuNR.

Here we combine $Cd_xSe_yZn_{1-x}S_{1-y}$ gradient core shell quantum dots (QDs) and gold nanorods (NRs) by self-assembly process in aqueous solution. Dramatic two-photon excitation luminescence enhancement with fast decay has been observed in time-resolved photoluminescence (TRPL) experiment. In TRPL measurement, two-photon excitation luminescence of QDs+AuNRs shows much faster multiple decay process than QDs. This indicates multiple layers of QDs around AuNRs structure is formed, which is consistent with TEM measurements.

Stochastic variational approach to polaron formation dynamics in molecular aggregates

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Redfield relaxation theory is widely used to describe the excitation population dynamics in optically excited molecular aggregates. However, a large number of such systems fall beyond the parameter range for which the Redfield approximation is justified: either the interaction between the system and its local environment is strong, or the environment correlation timescale is large (non-Markovian regime). Both of these cases induce transition from purely excitonic picture to hybrid exciton-phonon states (excitonic polarons) [1].

To study the transition dynamics we use a stochastic version of a time-dependent variational method with the Davydov Ansatz. While normally it only considers the zero-temperature case we extend the model with sampling of environmental initial states, enabling us to model the dynamics at finite temperatures. The approach allows us to obtain a wide range of observables, ranging from single-wavefunction level quantities, such as delocalization factor, to spectroscopic signals, such as time-resolved fluorescence (TRF). Computational costs are low compared to exact approaches, and no restrictions apply to the form of environmental spectral density.

We apply the model to describe the excited state evolution and polaron transition dynamics in the B850 ring of the LH2 molecular aggregate. Although the polaronic effects can be quantified, we find that they produce no easily discernible effect on the TRF spectra with the used set of parameters [2].

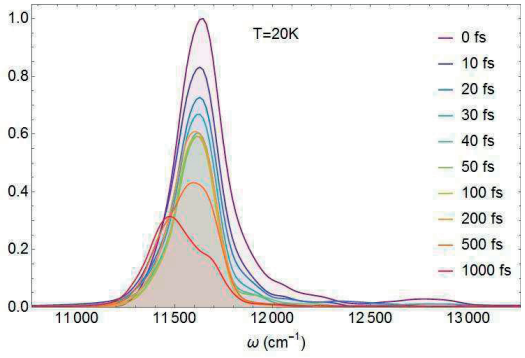

Fig.1. Simulated time-resolved fluorescence spectra of the B850 ring of LH2

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Origin of the LH2 to LH3 850 -> 820 nm absorbance blue shift

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Light harvesting (LH) complexes are responsible for the capture, transfer and exploitation of solar energy in several families of bacteria. The most common of such complexes, denoted LH2, is characterized by a barrel-like arrangement of protein's alpha helices, which provide scaffolding for the chromophores, namely carotenoids and bacteriochlorophylls (BChls). The BChls are arranged into two rings, constituted by 18 and 9 units and indicated as B850 and B800, following their characteristic near-IR absorption peaks. These rings, their characteristic absorptions, and their capability to efficiently transfer the absorbed light's energy, represent one of the most studied, both theoretically and experimentally, photochemically active, biological systems.
A naturally occurring variant of LH2, called LH3, presents the same general structure, but shows a blue-shifted absorbance peak from 850 to 820 nm. In our hypothesis, subtle differences in the protein scaffolding promote different BChl conformers, with accordingly different absorption wavelengths. Excitation energies for BChls extracted from the crystal structures of both LH2 and LH3 were computed with MS-RASPT/SA-RASSCF and TD-DFT. The calculations reveal that indeed a change in conformation of the BChl macro cycle ring (as exemplified in Figure 1) is responsible for a strong blue shift (90 nm) of the first absorption band. The coupling with the other chromophores in the protein complex is likely to regulate the intensity of such blue shift in the overall complex.

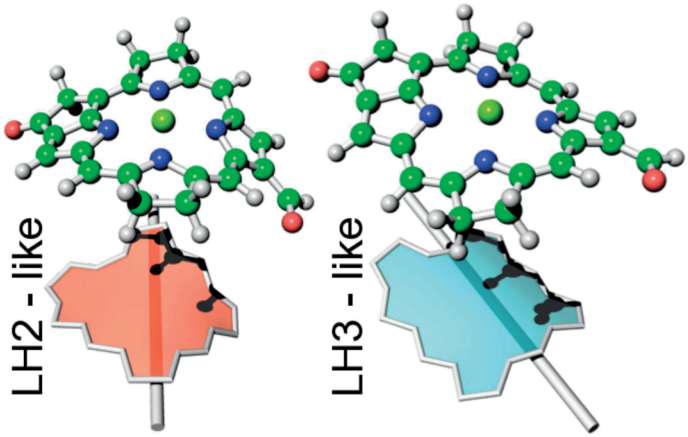

Fig.1: exemplification of the conformational change responsible for bacteriochlorophylls' blue shift

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Photoluminescence microscopy of individual organometal halide perovskite nanowires: effect of crystal-phase transition

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Organometal halide $CH_3NH_3PbI_3$ perovskites are attracting increasing attention as very promising materials for solar cells, light-emitting diodes and laser devices. Organic-inorganic halide perovskites possess properties of traditional inorganic semiconductors, combined with the great advantage of low-cost solution processing. Their exceptional solar energy conversion and emission performance are driven by long carrier lifetimes, high carrier mobility, strong broadband optical absorption and high fluorescence quantum yield with possibility to tune the emission wavelength. Recent structural and photophysical studies concluded that $CH_3NH_3PbI_3$ has two accessible crystal forms below room temperature: a tetragonal phase from 160 K to room temperature and an orthorhombic phase for temperatures *T* below 160 K. The purpose of this work is to investigate effect of crystal-phase transition on luminescence properties of $CH_3NH_3PbI_3$ perovskites using optical microscopy techniques.

We studied $CH_3NH_3PbI_3$ nanowires (NWs) grown by a surface-initiated solution fabrication method. Scanning electron microscopy has shown that resulting NWs had length up to 4 μm and diameter varying from 100 to 500 nm with flat rectangular end facets indicating high-quality single crystal structure. Temperature-depended steady-state and time-dependent micro-photoluminescence measurements on the individual NWs were performed in temperature range of 77 – 295 K. Photoluminescence microscopy combined with spectroscopy allows us to study the local variations of photophysical properties in a single NW with high spatial resolution.

Fluorescence microscopy of single $CH_3NH_3PbI_3$ NWs at different temperatures reveals the coexistence of the tetragonal and orthorhombic phases in $120\ K < T < 160\ K$. For the first time, temperature-dependent luminescence intensity variation along NW axis induced by crystal phase transition was observed. Emersion of bright areas at the temperature region of the phase transition may be attributed to small inclusions of domains of the room-temperature phase. The photoluminescence enhancement observed at around 150 K is due to decreasing of quenching volume of the traps and increasing of the PL intensity from the tetragonal phase with the narrower band gap, in which a large fraction of photoexcited carriers agglomerate. Processes of carrier diffusion between domains of different phases and spatial carrier localization are discussed.

This effect can be potentially beneficial for optoelectronic device applications for emission enhancement in LEDs and decrease of the gain threshold in lasers.

Optical Characterization of Pnictogens Based Cyclopentadithiophene Complexes

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The world demand for energy is tremendously increasing. It is expected to triple by the end of the century (*1*). Large effort is currently aiming to cover this need and to find a reliable and sufficient supply of energy by looking for alternative sources. Several requirements have to be considered in the research of the new materials beside high efficiency: stability, human-environment safety and the low cost. In this context, a set of novel semi-conductor materials based on the alkenes in combination with Arsenic (As) and Phosphor (P) show promising features as they are stable under environmental conditions and can be generated in a single step printing process without dangerous precursors or extensive heat treatment. In order to control and tune these materials, a good understanding of their properties is required. Herein, we investigated the role of As and P incorporated into a cyclopentadithiophene (CPDT) base structure in the photo induced processes, and the effect of their coordination towards an attached gold atom. The incorporation of these pnictogen elements increases the electron acceptancy of the double bond at the bridgehead position of the CPDT fragments. This gives in addition to the stabilization of the lowest unoccupied molecular orbital (LUMO) level rise to potential applications in opto-electronics materials (*2*). Optical pump probe spectroscopy revealed the fast dynamics (~10 ps) occurring upon excitation from the highest occupied molecular orbital (HOMO) to the LUMO one. While the choice of the pnictogen element has only a minor influence on the relaxation the addition of the gold atom extends the lifetime to the ns timescale. Density functional theory (DFT) calculations supported by electrochemical studies clearly lay the HOMO and LUMO over the Alkene and the CPDT including the sulfur (*3*), a configuration allowing the selective probing of these states by time resolved x-ray spectroscopy.

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Ultrafast dynamics investigations of Au colloidal nanoparticles

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The ultrafast dynamics of Au colloidal nanoparticles functionalized with cysteine ligands is investigated experimentally following excitation with femtosecond laser pulses. The transient absorption signal presents a bleaching of the surface plasmon band and a transient absorption at the wings of the band. The kinetics of the "hot" electrons in Au nanoparticles [1] is investigated using two methods: (i) fitting specific kinetic traces with a double exponential function and (ii) global target analysis of the entire spectrum [2]. We developed a method for measuring the instrument response function and the frequency chirp of the white-light continuum (WLC) pulses and used it for global target analysis. The method is based on inducing the optical Kerr effect [3] in different solvents and in the empty quartz cuvette. The results for Au nanoparticles show a fast component of around 1 ps and a slower one of approximately 300 ps. The increase of the ligand concentration produces a variation of the relaxation times, as well as a delay of the time zero kinetics due to the adsorption of the ligands to the Au surface.

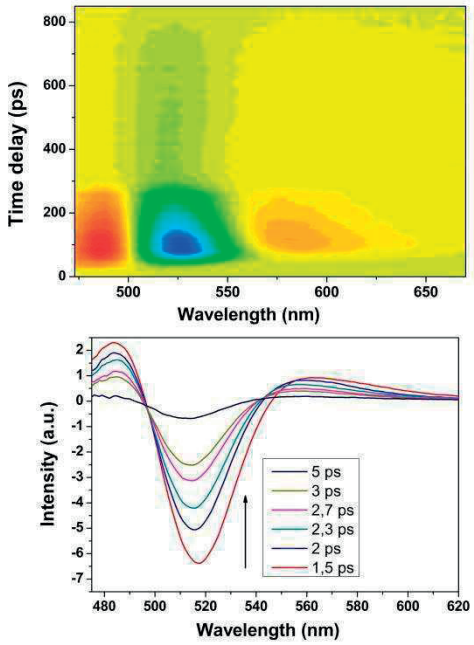

Fig.1. 3D data carpet and transient absorption spectra of the colloidal gold nanoparticles showing the bleach recovery of the ground state as a function of time delay between pump and probe pulses (the arrow indicates the time increase). Excitation at 440 nm.

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Transparent CoO_x/nano-ITO film for water oxidation with high TOF

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Photoelectrochemical conversion of solar energy into chemical fuels is considered as an attractive approach to solve the energy crisis.[1,2] Based on the traditional synthesis methods, most PEC devices employs metal oxide with agglomerated nanostructures catalysts for water oxidation. Generally, TOFs of these catalyst is very low (less than 0.1 s^{-1}), which leads to the low utilization of metal.[3] Here, via the molecular absorption coupled with calcination method, we construct a transparent CoO_x/nano-ITO film with highly dispersed Co active sites, which exhibits extremely high TOF for catalytic water oxidation. Firstly, a Co based molecular catalyst is absorbed on nano-ITO surface. Then, the device is calcinated to remove the organic ligand, leading to the formation of Co active sites. Electrochemical water oxidation activity of the obtained CoO_x catalyst was studied in 1M KOH solution. TOF of 27.1 s^{-1} is achieved at 480 mV overpotential, which is much higher than other reported metal oxide, including even precious metal based inorganic catalyst. Furthermore, the CoO_x/nano-ITO film showed totally transparent property, because of the low UV-Vis absorption of the highly dispersed CoO_x catalyst. The advantages of high activity and transparent property lead the film to be a good candidate for fabricating of efficient photoelectrochemical devices with high activity and superior quantum efficiency.

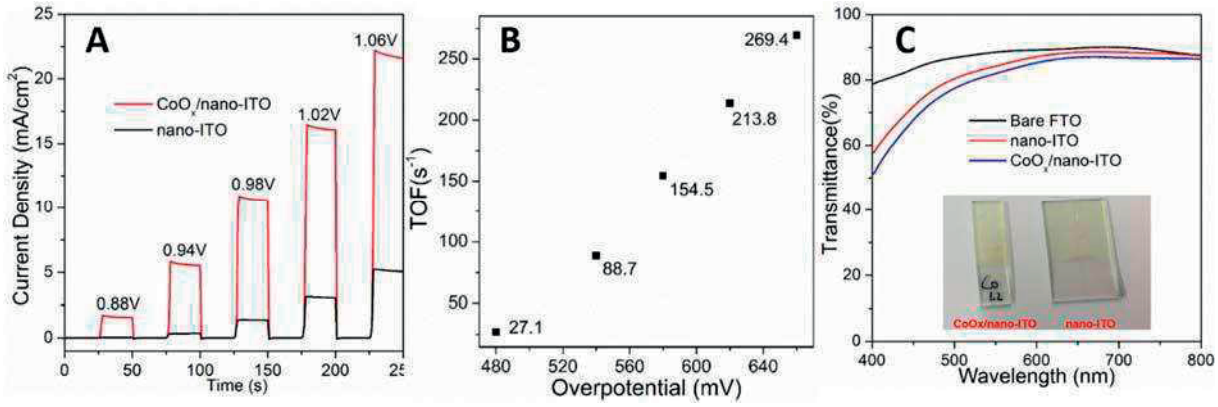

Fig.1. (A) Chronoamperometric current densities measured in 1M KOH buffer (pH 14) at CoO_x/nano-ITO (red) and nano-ITO (black) under the application of sequential potential steps. (B) TOF plot of CoO_x/nano-ITO electrode as a function of overpotential. (C) UV-Vis spectra of bare FTO, nanoITO on FTO and CoOx/nano-ITO, the inset is the picture of CoOx/nano-ITO and nano-ITO

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Time resolved spectroscopy of a Ruthenium-Based Molecular Catalyst−Porphyrin−Fullerene-Linked Pentad

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Artificial photosynthesis using sun light as energy source and water as an abundant electron source to produce fuels such as hydrogen is a promising concept to meet future energy demands. In this study, we investigate an electron acceptor – sensitizer – water oxidation catalyst system combining the photosynthetic functions light harvesting, charge separation and water oxidation.

This poster will present the photophysical properties of a molecular Ru − $(C_{60}$ − ZnP$)_2$ pentad. Two zinc porphyrin (ZnP) − fullerene (C_{60}) linked dyads for efficient charge separation (1) were linked to a Ru based WOC (2).The initial charge separation processes after selective excitation of the ZnP moiety were investigated by UV/VIS time resolved transient absorption measurements in the femtosecond to nanosecond time regime. The data show a charge separation between the ZnP and the C60 with a time constant of tens of picoseconds followed by a charge shift of the hole from the ZnP to the Ru catalyst with a 40 nanosecond time constant.

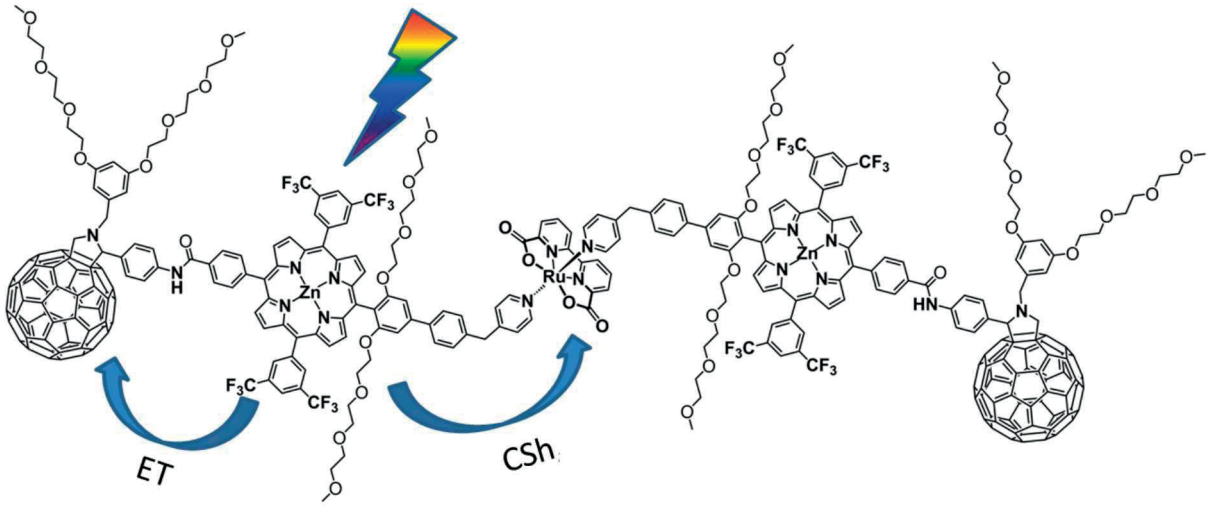

Fig.1. Investigated **Ru− $(C_{60}$−ZnP$)_2$** pentad and observed processes after excitation of the ZnP moiety.

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Exciting a more energetic light, and splitting the quantum

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Up beyond blue where photons are few, with wavelengths as short as an atom, is the chemist's great chance to watch molecules dance; while physicists help make it happen. The field of chemical structural dynamics using pump-probe X-ray techniques has been brought to fruition by many collaborations between chemists and physicists in recent decades. Such collaborations have led to mutual advances in the developments of concepts, sources, sample excitation, detectors, experiment topologies and diverse modelling capabilities; with spinoffs for both major disciplines. Among the insights that have come from it is the curious business of using moderate energy photons to construct high energy photons, interacting them with matter, and then disintegrating them into huge numbers of low energy excitations. These exercises in the thermodynamics of colour have avoided the primary cause of flux loss in traditional high resolution X-ray spectroscopy. They have been undertaken to enable observation of fundamental molecular machinations within the chemical laser laboratory, where the action can be excited and stroboscopically observed with great finesse using ultrafast light pulses. A handful of key developments will be presented in this field of chemical physics, that the author has been privileged to be part of since the early 1990s.

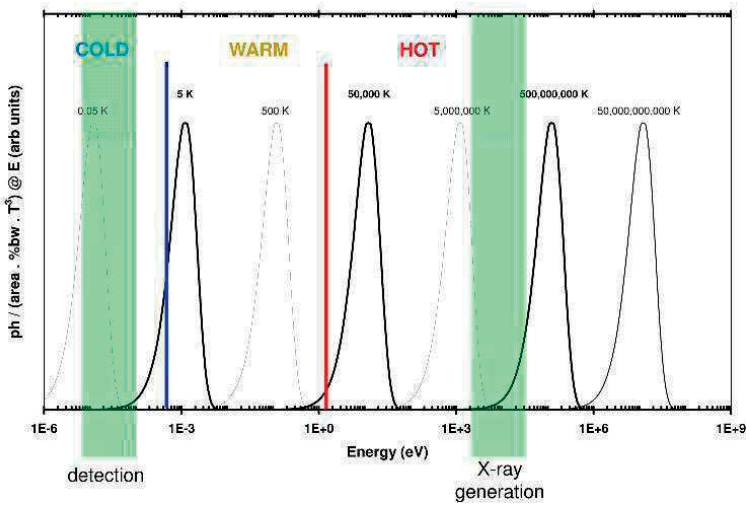

Figure: normalised Planck distributions, showing the range of effective temperatures and photon energies associated with laboratory-based X-ray approaches. (From a 2008 “Hot, Warm, Cold” seminar by the author, and used on Lund’s Chemical Physics X-ray webpage since then.)

Effect of Hole Transporting Material on Charge Transfer Processes in Zinc Phthalocyanine Sensitized ZnO Nanorods

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The photoinduced electron transfer processes were studied in hybrid systems consisting of a monolayer of zinc phthalocyanine (ZnPc) assembled on ZnO nanorods and a film of organic hole transporting material (HTM) atop.[1] Poly(3-hexylthiophene) (P3HT) or Spiro-OMeTAD were used as HTM. The study was carried out by ultrafast transient absorption spectroscopy technique with selective excitation of ZnPc at 680 nm or P3HT at 500 nm. Data analysis revealed that photoexcitation of ZnPc in the structure ZnO|ZnPc|P3HT results in a fast (1.8 ps) electron transfer from ZnPc to ZnO which is followed by a hole transfer from the ZnPc cation to P3HT roughly in 30 ps. However, in the case of ZnO|ZnPc|Spiro-OMeTAD structure, the primary reaction upon excitation of ZnPc is a fast (0.5 ps) hole transfer from ZnPc to Spiro-OMeTAD, with following electron injection from the ZnPc anion to ZnO in roughly 120 ps. The results are summarized schematically in Figure 1. This study demonstrates how two structurally very similar hybrid architectures implements two different mechanisms for photoinduced charge separation found in dye-sensitized or in organic solar cells.

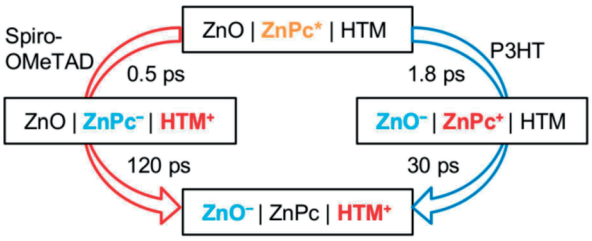

Fig.1. Scematic illustration of the main charge generation mechanisms in the studied systems.

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2D Electronic Spectra of Marcus Electron Transfer

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Coherent multi-dimensional spectroscopy enables direct measurement of the coherences associated with dynamic processes in photochemical systems. Most experiments have reported on energy migration, often in photosynthetic antenna systems. A few recent papers discuss electron transfer.

Based on a Keldysh contour formulation of four-wave mixing spectrosopy (1), recently extended to include molecular vibrations, we discuss theoretically the coherent features of the prototypical electron transfer – Marcus electron transfer.

The quantum coherences of electronic processes provide a new window into mechanistic understanding. These prospects will be discussed.

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Sulphur Kα emission spectroscopy with a table-top x-ray source and a transition-edge energy dispersive detector

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Thiophenes are among the many important base blocks of organic light harvesting mechanism. Together with problems in the oil and steel industry, this well motivates the study of sulphur as atomic sensor. However, x-ray spectroscopy in “tender” energy range is a challenge. We address this quest by conjugating a table-top x-ray source and an energy dispersive x-ray detector for measurements in both the soft and hard x-ray ranges.
Recently we have developed a table-top laser plasma x-ray source which can generate broadband bremsstrahlung radiation from 2 keV to 12 keV, with short (sub-picosecond) characteristics pulses and a flux of 200 photons/shot/sr at 5.9 keV. In addition that, we have achieved 3.6 eV (FWHM) energy resolution at 5.9 keV and ~2 eV FWHM for sulphur Kα line (2.3 keV) with a 160-pixel array of superconducting transition edge sensors. This table-top wide-range x-ray source and high resolution x-ray detector enable us efficient measurements of the soft and hard x-rays at the same time, and thus resulting in more comprehensive information about the structure and reaction dynamics in samples under investigation.
In this poster, we present the details of our x-ray source and detector, and discuss the future measurements and science impacts.

Rearranging from 6- to 7- coordination initiates the catalytic activity – An EPR study on a Ru-bda water oxidation catalyst

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Interest for solar energy conversion is growing rapidly along with the ever increasing energy demand worldwide. Production of hydrogen as a green and renewable fuel from water splitting process is now percieved as one of the most interesting concepts to solve the energy crisis.

In 2009, Sun et al reported an efficient ruthenium-based catalyst, Ru-bda (H_2bda =2,2´bipyridine- 6,6´-dicarboxylic acid), for water oxidation reaction. Despite of the amazing improvement in catalytic activity along the past years, a lack of understanding on the water coordination remain. In this work, we report our EPR and DFT studies on a Ru-bda complex at its Ru^{III} oxidation state, which is the initial state in the catalytic cycle.

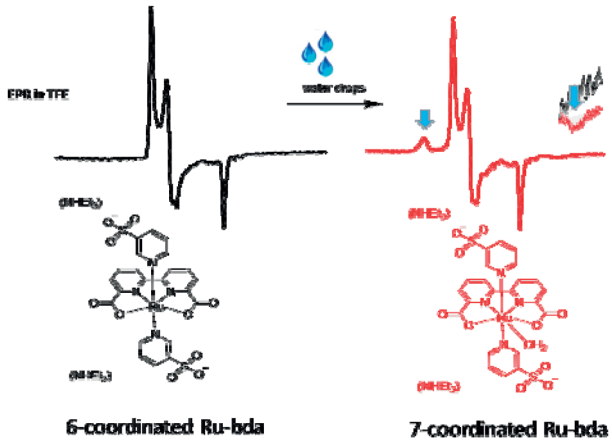

Fig.1. The formation of the 7-coordinated Ru-bda displayed in EPR

Our investigation suggests that already at this state there is a rearrangement in the ligand sphere where coordination of a water molecule at the 7th position takes place under acidic condition (pH = 1.0) to form a rare 7- coordinated Ru^{III} species.

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Signal amplification and transduction in phytochrome photosensors

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Phytochromes are multidomain red light photosensor proteins, which convert red light photons to biological activity utilizing the multitude of structural and chemical reactions. The steady increase in structural information obtained from various bacteriophytochromes has increased understanding about the functional mechanism of the photochemical processes of the phytochromes. Furthermore, a number of spectroscopic studies have revealed kinetic information about the light-induced reactions. The spectroscopic changes are, however, challenging to connect with the structural changes of the chromophore and the protein environment, as the excited state properties of the chromophores are very sensitive to the small structural and chemical changes of their environment. In my contribution, I introduce our present knowledge about connecting spectroscopic results with structural details of signaling process of phytochromes.

Photocurrent detected two-dimensional spectroscopy of semicondcutors

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Photocurrent detected two-dimensional spectroscopy is used to study the effect of excitations in InP nanowire array solar cell. Results show instantaneous changes in the band structure of the semiconductor material due to the excitation of electrons into the conduction band. Possible mechanisms that lead to the changes are discussed.

The measured band gaps of semiconductors decrease when the conduction bands are populated by electrons.[1] Recent, studies indicate that the change in the band gap occurs in sub femtosecond time scale preceding lattice relaxation.[2] However, the reasons behind this reduction in the band gap have not been well understood. We have used photocurrent detected two-dimensional spectroscopy[3] to investigate this phenomenon. Our experiments on InP nanowire array solar cells also indicate that the band gap reduction is instantaneous at high excitation densities. We also observe modulation in the band structure, which indicates the prevalence of dynamic Franz-Keldysh effect in such solar cells. The results show that different nonlinear field matter interactions in photoactive devices can have effects in the photocurrent from the device, and such effects could be used to investigate the changes in the electronic structure of the devices under different operating conditions.

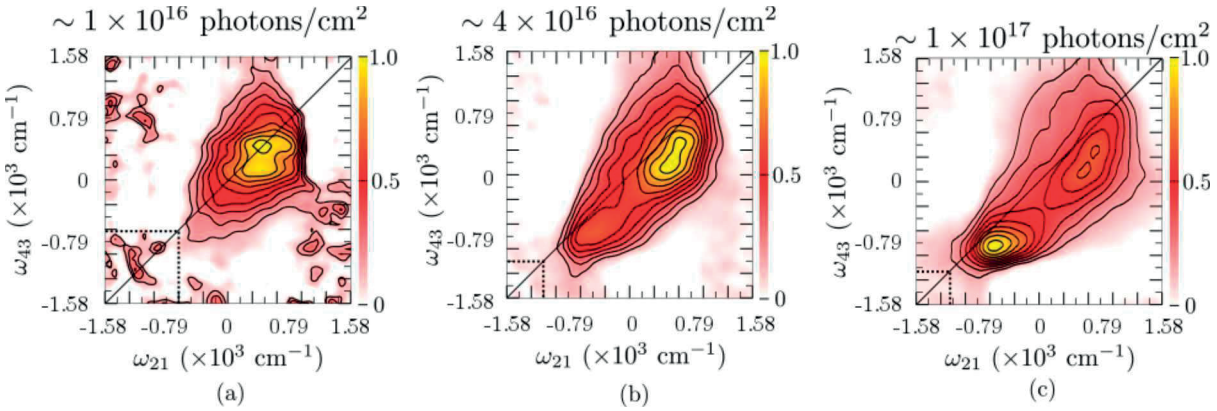

Fig.1 Photocurrent detected two-dimensional spectra at zero population time of InP nanowire array solar cell at different excitation densities (a, b and c). The frequency axes are labeled relative to the reference frequency at 12675 cm^{-1} (788 nm). The band gap at low excitation density as estimated from (a) is at 12042 cm^{-1} (830 nm). At high excitation densities (b and c), the band gap decreases to 11561 cm^{-1} (865 nm). We also observe strong modulation of the band structure in (b) and (c) owing to dynamic Franz-Keldysh effect.

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Internal Conversion in Cyclic Ketones: Exploring the Relation between Structure and Internal Conversion using Photoelectron Velocity Map Imaging

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Electronically excited molecules have several options to dispose of the excess energy and return to the ground state. One possibility is to transform the electronic energy into vibrational energy – a non-radiative process known as internal conversion (IC). IC processes are often well-described by statistical models, such as Fermi's Golden Rule, in which a high density of final states accelerates the process. However, Fermi's Golden Rule is not always applicable and it is not well-suited to describe IC processes when they occur on a femto- to a few picosecond timescale. Such ultrafast IC has been shown to involve a restricted subset of vibrational modes, in other words it is a non-statistical process (1). In fact the non-statistical nature of the process in many cases ensures the photostability of e.g. biomolecules (2). Several investigations have indicated that the IC rate is dependent on the molecular structure (3). This relationship is however not well understood and one open question is whether it involves all types of chromophores, another is how it changes when combining chromophores.

This contribution aims to elaborate on this relationship between structure and rate by investigating the $S_2 \rightarrow S_1$ IC in cyclopentanone, 2-methylcyclopentanone, cyclohexanone and 2-cyclohexenone. Using photoelectron velocity map imaging spectroscopy we can identify the Rydberg character of the initially excited S_2 state and follow its conversion into the S_1 state. Despite the higher density of states in cyclohexanone compared to cyclopentanone, the smaller system undergoes IC faster and thereby manifests the non-statistical nature of the IC process. Adding a methyl group at the 2-position further increases the IC rate compared to cyclopentanone. The mechanism behind the faster IC in cyclopentanone compared to cyclohexanone, as well as the effect of adding the methyl substituent and another chromophore (a double bond) will be explored.

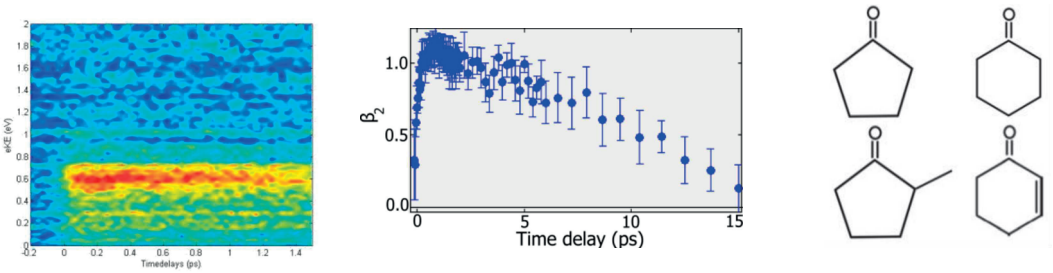

Fig.1. Photoelectron spectrum of the first few femtoseconds of cyclopentanone (left). Anisotropy parameter (β_2) of the Rydberg peak (centre). The four investigated molecules (right).

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2D Spectroscopy of CdSe Quantum Dots

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Quantum dots are semiconductor nanocrystals whose size leads to quantum confinement of charge carriers, manifesting as optoelectronic properties such as a size-tunable band gap, quantized energy levels and multiple exciton generation under the right conditions (*1*). If quantum dots are to be used as efficient light harvesters in solar cells, these properties have to be understood.

We perform 2D electronic spectroscopy of colloidal CdSe quantum dots at room temperature and at 77 K. The results reveal a rich electronic structure with a number of cross peaks showing the connections between the levels. Absorption bleach is the major contribution for the lowest excitonic transition (see figure). By the analysis we gain important information about coupling between various excitonic states, which is essential knowledge to track the energy flow in the excitonic states after light absorption.

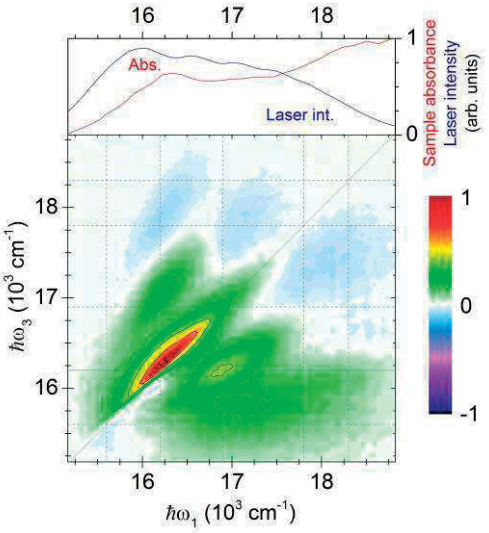

Fig.1. Total real 2D spectrum of 7.1 nm CdSe QDs in methanol/ethanol glass at 77 K, at population time 10 ps; laser and absorption spectra. The diagonal line marks where $\hbar\omega_1 = \hbar\omega_3$; the horizontal and vertical lines mark the energy levels.

We unambiguously identify the lowest state as an optically allowed hole trap, and identify an electron trap with excited-state absorption. The presence of traps changes the initial dynamics entirely by offering a different relaxation channel. 2D electronic spectroscopy enables us to pinpoint correlations between states and to easily separate relaxation from different starting states. The high resolution of our setup also makes it possible to measure large QDs with closely spaced states, letting us cover several states. We observe direct rapid trapping of $1S_{3/2}$, $2S_{3/2}$, and $1S_{1/2}$ holes, and several competing electron relaxation processes from the $1P_e$ state.

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Ultrafast structural dynamics of a photocatalytic model system

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Recent advances in femtosecond X-ray experimental techniques have opened up new possibilities in the study of the ultrafast photoinduced dynamics of complex molecular systems in the condensed phase. A detailed understanding of the underlying physical and chemical processes can only be attained with the help of theory and atomistic simulations to guide the interpretation of the experimental results.
In the present work we used our newly implemented QM/MM molecular dynamics (MD) method (*1*) to assist the analysis of ultrafast diffuse X-ray diffraction measurements in water solution of the binuclear metal complex $[Pt_2(P_2O_5H_2)_4]^{4-}$ (PtPOP). The experiments, which were realized at the LCLS X-ray free electron laser (XFEL) facility of Stanford by our group, exploited the wavelength and bandwidth of the pump pulse to track the coherent vibrational dynamics along the Pt-Pt stretch coordinate arising after creation of a "hole" in the ground state population: a direct observation of ground state structural dynamics.
Our MD code, which combines the efficiency of the DFT-GPAW method (*2*) with the electronic embedding of the metal complex in a system of point charges representing the solvent, enabled us to collect the statistical quantities necessary to propagate non-stationary nuclear distributions, from which the instantaneous scattering can be calculated (*3*). Direct comparison with the experimental transient signal provides a useful means to interpret the data. Furthermore, solvent shell changes, which have an important role in ultrafast energy and phase relaxation, were characterized. Overall, it was possible to acquire an accurate mechanistic insight into the processes of vibrational energy relaxation and coherence decay which govern the experimentally observed ultrafast dynamics.

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Mechanical Characterization of Wurtzite InP Nanowires Using Phonon Spectroscopy

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Nanowires are widely studied for their unique and tunable physical and chemical properties. For piezoelectric application and nano-electromechanical systems (NEMS), knowledge of mechanical properties of nanowires is crucial. Moreover, some material, such as InP in wurtzite crystal structure, can be stable only on nanoscale and their properties, in particular mechanical, are unknown. Thus, it is important to find a suitable method for mechanical characterization of nanostructures.

In this study, we used the picosecond ultrasonic technique, in which a sub-picosecond laser is used to excite the sample, generating electron-hole pairs. The excess energy of the photo-excited carriers is transferred to the lattice, generating coherent lattice vibrations called phonons. The phonons interact with the probe light and cause oscillations in the transient reflectivity signal (inset of Fig. 1. a), enabling monitoring of the phonon propagation.

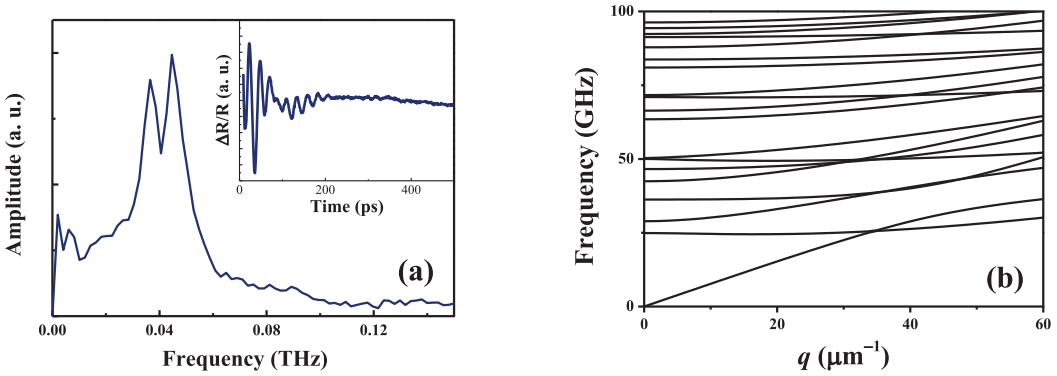

Fig.1. a. Fourier transform of phonon dynamics in InP nanowire. Inset is the experiment data. b. Calculated dispersion relations of InP nanowires

Here, we applied the picosecond ultrasonic technique to InP nanowires with wurtzite structure. We observed oscillations in the transient reflectivity, and corresponding phonon frequencies were revealed by Fourier transform. Multiple phonon modes, both propagating and confined, were observed in the nanowires. We use three-dimensional mechanical algorithm to analyze and simulate the vibration of a nanowire [1], and obtain the dispersion relations, which are very different from that in bulk materials, as shown in Fig. 1 b. By fitting the dispersion relations to the frequencies obtained experimentally, we can extract the elastic constants of the wurtzite InP. This technique is a non-destructive, complete mechanical characterization method and can be applied to any nanowire.

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Altering the electron transfer in hydrogenases for photobiological hydrogen production.

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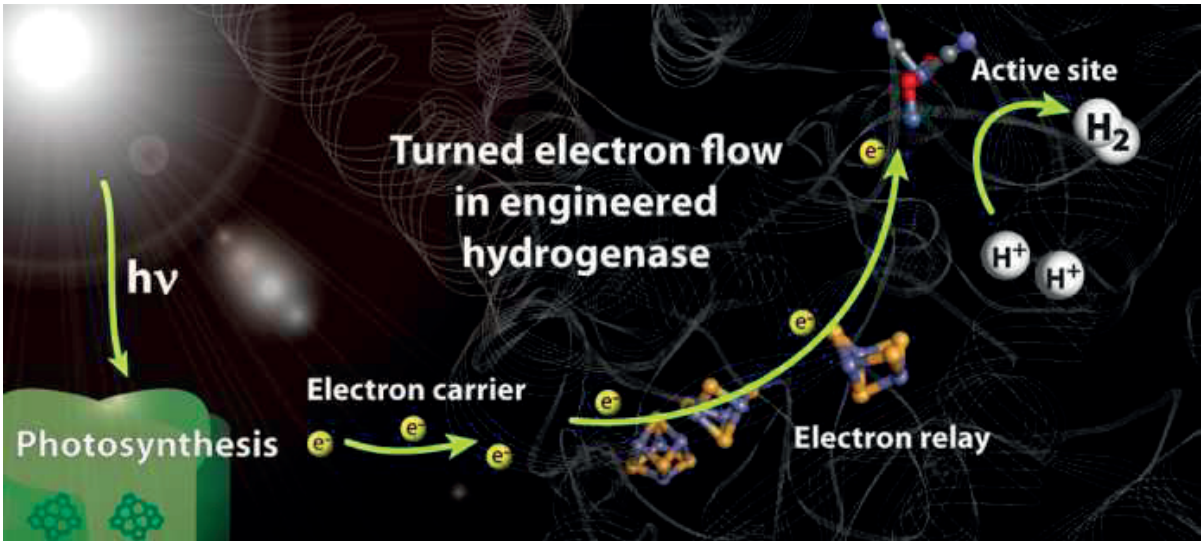
Hydrogen can be produced in a sustainable manner via photosynthesis using nitrogen-fixing cyanobacteria, where H_2 is produced by the enzyme nitrogenase. However, the evolved H_2 is readily oxidized by the uptake hydrogenase HupSL. We have developed a novel strategy to circumvent this issue. By engineering the electron transfer chain in HupSL from Nostoc punctiforme, the enzyme was altered from a hydrogen uptake enzyme to become a net H_2 producer. *N. punctiforme* containing the engineered HupSL exhibited sustained, light-dependent H_2 production over the course of several days. EPR spectroscopy showed that the protein engineering resulted in a conversion from a [4Fe–4S] to a [3Fe–4S] cluster in the proximal site, most likely affecting the redox balance of the electron transfer chain, and effectively reversing the electron flow within HupSL. The interdisciplinary nature of the present work allowed connecting knowledge at the molecular level with the energy metabolism in a real system, and paves way for development of robust H_2-producing cyanobacterial strains.



The Role of Vibrational dynamics in Electronic Relaxation of $Cr(acac)_3$

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Ultrafast energy relaxation of $Cr(acac)_3$ dissolved in tetrachloroethylene (TCE) is studied by time resolved infrared (TRIR) spectroscopy by using electronic and vibrational excitation. After electronic excitation at 400 or 345 nm, the ground state recovers in two time scales: 15 ps (major pathway) and 800 ps (minor pathway), corresponding to fast electronic transition to the ground state and intermediate trapping on the long-lived ^{2}E state followed by intersystem crossing (ISC) to the ground state. The quantum yield for the fast recovery depends on the excitation wavelength, being higher for 345 nm. Vibrational cooling (VC) occurs in the electronic excited states with a time constant of ~8 ps and on the ground electronic state with a time constant ~12 ps, indicating that ground state recovery after electronic excitation is not limited by VC. A kinetic model is presented which explains the observed dynamics. The key point of the model is that the ground state recovery occurs via thermally activated back-intersystem-crossing (b-ISC) to the quartet manifold presumably via multiple curve crossings which are sampled while the system is vibrationally hot. This underlines the importance of vibrational cooling as a determining factor for the electronic relaxation chain. Vibrational excitation of the νC=C and νCO vibrations revealed fast subpicosecond (300 – 700 fs) intramolecular vibrational redistribution (IVR) process from the localized vibrational states to the bath of vibrational excitations.

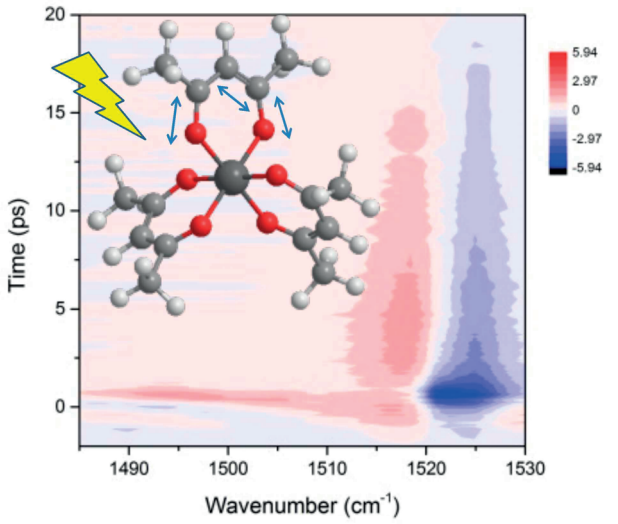

Fig.1. Transient infrared absorption signal after the broadband IR excitation.[1]

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Terahertz conductivity in semiconductor nanostructures

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Terahertz (THz) spectroscopy constitutes a suitable non-contact method for probing nanoscopic motion of charges with a sub-picosecond time resolution. Although ultrafast THz photoconductivity is routinely measured, its relation to charge transport in nanostructured semiconductors is still poorly understood on the microscopic level. In this contribution, we will review our theoretical description, which includes (i) interaction of mobile charges with nanoparticles boundary, and (ii) screening of the incident THz pulse by depolarization fields.
The response of charges to the local electric field is calculated by Monte-Carlo simulations of quasi-classical carrier thermal motion which involve parameters like nanoparticle size or coupling between nanoparticles (*1*). These results will be confronted with quantum mechanical calculations of the response of isolated nanoparticles. The depolarization fields are accounted for using an effective medium approximation: we show that for most nanostructures, only the percolation degree is important whereas further details of the morphology play only a minor role (*2*).
Results on selected systems will be presented: these include namely Si nanocrystals prepared by thermal decomposition of Si-rich layers (Fig. 1) (*3*) or Si nanocrystals formed by electrochemical etching of Si wafer (*4*). In the analysis, scaling of the effective conductivity with optical excitation intensity provides information on the percolation degree while parameters of charge transport are determined from the spectrum at low excitation intensities.

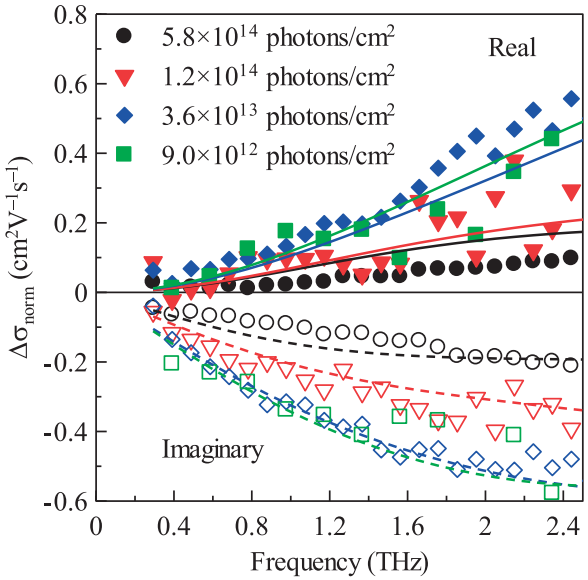

Fig 1. Silicon nanocrystals prepared by thermal decomposition of $SiO_2/SiO_{0.64}$ superlattices: spectra of effective transient conductivity normalized by charge density [$\Delta\sigma_{norm} = \Delta\sigma/(e_0 n_{exc})$; $\Delta\sigma$ is effective transient conductivity, n_{exc} is excitation density)]. The decrease of $\Delta\sigma_{norm}$ with increasing excitation intensity shows that the nanocrystals do not form a long-range percolation network. The pronounced increase of the real part with frequency is incompatible with the 3.5-nm average size of nanocrystals observed in TEM images, but it points out to the existence of 40-nm sized nanocrystal clusters which have a dominant contribution to the sample photoconductivity. Symbols: measured data; lines: global fit with three adjustable parameters (cluster size, fraction of nanocrystals in clusters, and percolation strength).

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Intermediate Species of the Water Oxidation on the Platinum Investigated by Vibrational Spectroscopy.

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Hydrogen is a zero-emission fuel which has the highest mass energy density within the non-radioactive compounds. Immense effort in the field of photocatalytic water splitting strive to efficiently dissociate water into molecular hydrogen and oxygen using the sunlight. Heterogeneous catalysis on the solid-liquid interface seems to be a promising research direction (*1*).

Inorganic chemists synthetize myriads of catalysts investigating their catalytic activity. However, the mechanism of the photocatalytic process itself, together with the intermediate states involved remain mostly unknown. Attenuated total reflectence (ATR) spectroscopy and its time-resolved extension "two-dimensional attenuated total reflectance infrared (2D ATR IR) spectroscopy" is a structurally sensitive probe of the solid-liquid catalytic interfaces (*2*), which has the potential to shed light on the photocatalytic mechanisms.

Here we present steady state ATR and 2D ATR IR data of the hydrogen adsorbed species on the <3 nm thick platinum sputter coated layer in the water solution (Fig. 1). These experiments open up the possibilities to time-resolve the intermediate species and their dynamical evolution during the heterogeneous photocatalysis.

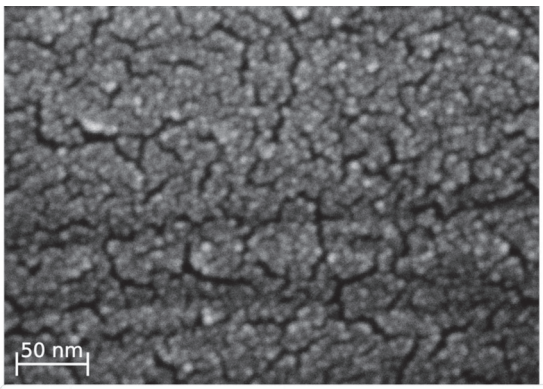

Fig.1. SEM image of a 2.5 nm thick platinum surface prepared by sputter coating.

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Spectroscopic studies of ultra-stable water-soluble ZnO nanocrystals: a new drawn for dye-sensitized solar cells

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ZnO was one of the first semiconductors used in dye-sensitized solar cells but its instability in aqueous media precludes its use for large-scale applications. Herein, we report on a novel ZnO nanocrystal material that is simultaneously stable and soluble in water due to its polyethylene glycol (PEG) shell strongly anchored to the inorganic core by carboxylate termini. The PEG shell also stabilizes the photo-generated hole, leading to a dramatic slowing down of charge recombination, which otherwise is a major hurdle in using ZnO. Sensitization of ZnO-PEG was confirmed by adding a natural organic dye (betanin).

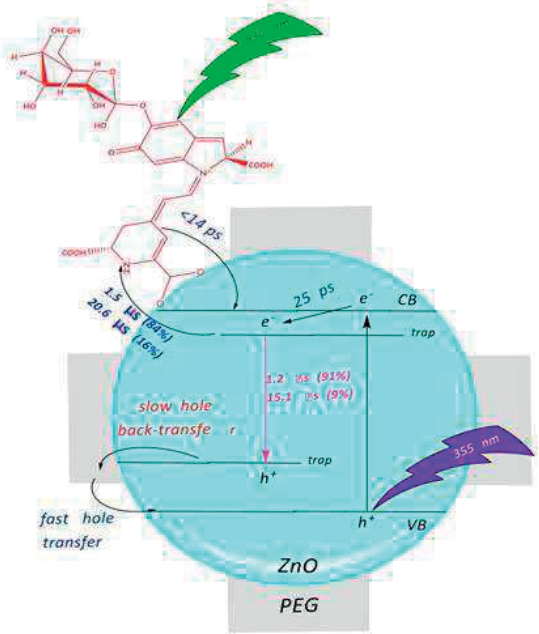

Fig.1. Schematic representation of charge transfers processes and associated time constants on betanin-ZnO-PEG system

Herein, we report on detailed spectroscopic characterization of ZnO NCs. Radiative recombination lifetimes were determined by time-resolved fluorescence spectroscopy. Starting with emission at 404 nm, the signal decays within 25 ps, which is the necessary time for the electron trapping into the shallow trap states below the conduction band. The emission signal at 560 nm was fitted with a modified stretched exponential and had two clear components a fast one (a time constant of 34 ns (67%)) and a slow one (2.2 µs (33%)) with the β value of 0.56. The electron lifetime in ZnO upon betanin excitation at 530 nm was monitored by fs and ns mid-infrared absorption spectroscopy. The electron remained in the conduction band suggesting that the charge stabilization mechanism must be associated to hole stabilization within the PEG shell. This is further corroborated by the time constants estimated from ns time-resolved mid-infrared absorption for ZnO direct band gap excitation. It should be mentioned that in both cases electrons survived in the conduction band up to seconds, which opens the perspective of using the system for solar fuel production.

Title

Temperature dependence of the far-red photochemistry in Photosystem II

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Abstract

In oxygen evolving photosynthesis, conversion of solar energy to chemical energy requires a sequential cooperative function between PSII and PSI. If a fairly even distribution of absorbed photons between PSII and PSI exists, then the system functions at maximum efficiency. At the far-red end of the spectrum however, the latter requirement has limitations. This is due to the spectral properties of the primary electron donors P_{680} at PSII and P_{700} at PSI where a small number of chlorophylls with absorption shifted to the far-red exist in the PSI antennae. This brings upon the well-known "red-drop" of the photosynthesis quantum yield above 700nm. The absorption limit of PSII was recently reported to extend into the far-red region, as far as 810nm at room temperature. It is noteworthy to explore if far red light and visible light drive the electron donation pathways similarly or if the partition ratio differs between the Y_Z/$CaMn_4$ pathway and the Cyt b_{559}/Chl_Z/Car_{D2} pathway. In this study, we report the temperature dependency of the electron donation in PS II induced by far red light between 77K and RT. The results clearly show difference in the temperature dependence of the Y_Z/$CaMn_4$ pathway and Cyt b_{559}/Chl_Z/Car_{D2} pathway and provide further inside on the nature of the oxidized primary donor in PSII upon far red illumination.

Quantum Photoelectrochemistry

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Investigations of emerging molecular and nanoscale solar energy conversion applications include first principles calculations of excited state evolution and photo-induced heterogeneous electron transfer processes.(*1*) Capabilities to investigate excited state evolution in light-harvesting metal complexes and hetero-bimetallic donor-acceptor systems beyond the initially excited Franck-Condon region are explored through calculations of manifolds of multidimensional potential energy surfaces (Figure 1a). (*2*) DFT and TD-DFT calculations of light-harvesting capabilities of promising donor-acceptor (D-A) polymers for bulk heterojunction solar cells provide opportunities to guide the development of polymers with improved electro-optical properties (Figure 1b). (*3*) Interfacial electronic interactions in dye-semiconductor interfaces are used to investigate long-range interfacial electron transfer in a spacer-mediated weak coupling limit (Figure 1c). (*4*) Particular focus is given to recent advances in the development and understanding of earth abundant light-harvesting materials using iron carbene complexes.(*5*)

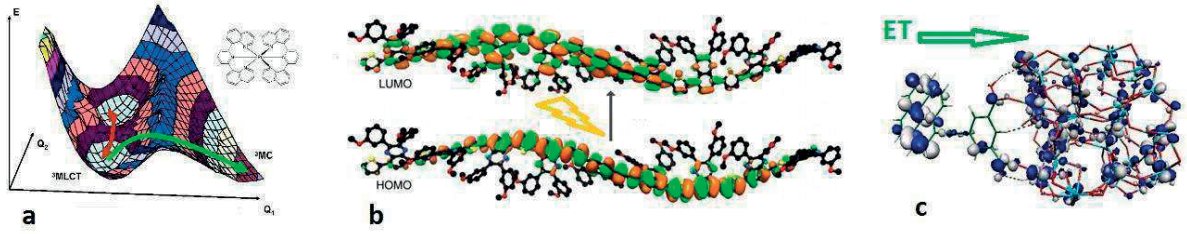

Fig.1. (a) Light-harvesting transition metal complex triplet PES, (b) D-A polymer excitation, (c) dye-sensitized nano-TiO2 interface.

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Understanding Charge Carrier Dynamics in Solar Cell Materials using Time Resolved Terahertz Spectroscopy

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The need for developing highly efficient solar cell devices have never been so pressing until recently when the urgency of using renewable energy sources becomes more evident. There are several promising technologies being explored by many groups with the sole purpose of optimizing harvesting sunlight and converting it to useful electricity. These include, but not limited to, dye- and quantum dot-sensitized, bulk heterojunction organic, inorganic nanowires, and very recently perovskite-based solar cells. In this talk, charge carrier dynamics of an assortment of solar cell technologies probed using time-resolved terahertz spectroscopy will be presented. Electron injection, mobility, charge carrier lifetime and recombination dynamics will be discussed.

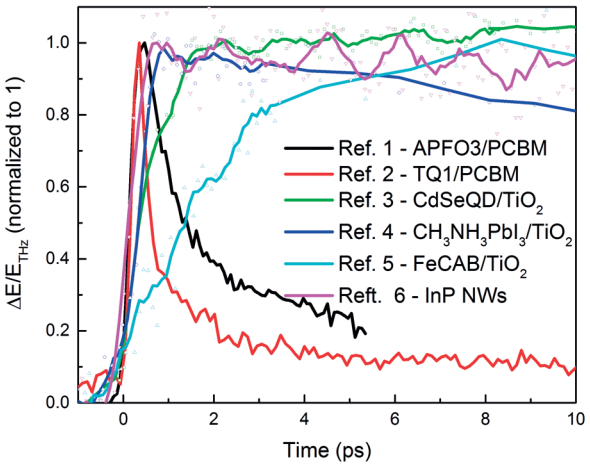

Fig.1. Early time THz photoconductivity kinetics of different solar cell materials showing characteristic times of photogeneration and recombination.

Shown in Fig. 1 is the early time THz kinetics of different solar cell materials normalized to unity. For bulk heterojunction materials, i.e. APFO:PCBM and TQ1:PCBM, an instrument limited rise is followed by a fast few picosecond decay. The rise is assigned to photogeneration of charges while the decay is due to charge pair annihilation brought about very high excitation density [1,2]. The rise time in the THz photoconductivity signal for CdSe quantum dot (QD) and perovskite CH3NH3PbI3 attached to TiO_2 appears to be slower than those of the organic-based materials. We note that since the response of the set-up is within the same timescale, interpretation of this rise is not straightforward. On one hand, the rise in CdSe/TiO_2 is followed by an almost constant signal. This is interpreted as electron injection to TiO_2 since non-attached CdSe showed fast decay at this timescale (details is found in Ref. 3). On the other hand, perovskite $CH_3NH_3PbI_3/TiO_2$ kinetics represents the hole left in the perovskite since electrons are injected in TiO_2 with very small signal (0.1 cm^2/Vs) compared to the estimated hole mobility of 7.5 cm^2/Vs. Finally, for InP NWs, the generation of charge carriers is also instrument limited. Details can be found in Ref. 5.

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Numerical study of the shell thickness dependence of the carrier injection rate from a core-shell quantum dot into a metal oxide

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Gradient-composition core-shell quantum dots are promising light absorbers for solar cell applications. This work is a follow-up on studies of the carrier injection from the quantum dot into ZnO nanoparticles. It is found experimentally that the hole injection rate from a quantum dot into a metal oxide is two orders of magnitude less sensitive to the shell thickness compared to the electron injection. In the picture of Fermi's Golden Rule, the carrier injection rate is proportional to the square of the matrix element of the coupling between the final and initial states. We therefore use the probability of finding the carrier outside of the quantum dot as a measure of the carrier injection rate into the metal oxide. We present the result of this model for six particular samples of different shell thickness with band structures constructed with data from experiments. In order to calculate the probability of finding the carrier outside of the quantum dot, we present a method for solving the time independent Schrödinger equation numerically, as an analytical solution does not exist for gradient core-shell quantum dots. As expected, the probability of finding the carrier outside of the quantum dot decreases exponentially as the shell thickness increases, however, we do not reproduce the experimental results for the difference in electron and hole injection rate.

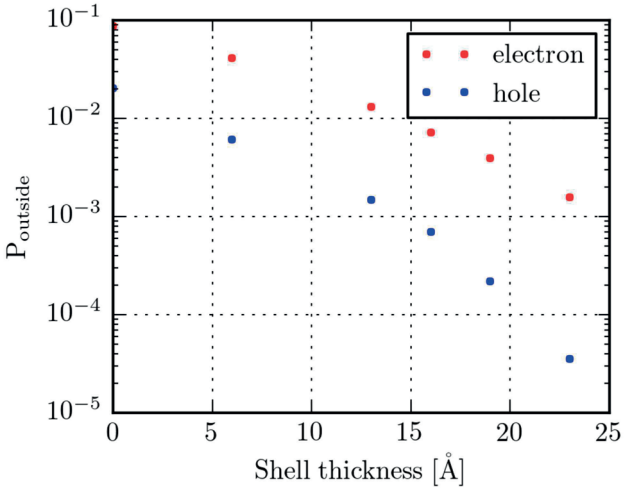

Fig 1: Probability of the carrier to be outside of the quantum dot for samples of six different thicknesses

Dissociation pathways of bound charge pairs at organic heterojunctions

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Free carrier generation mechanism in organic photovoltaic cells is not understood and actively debated. Energy gradient from interfacial to bulk states and carrier delocalisation have been suggested to drive charge separation but their contribution has not been quantified yet.

Here we combine broadband transient absorption spectroscopy with optical probing of carrier drift in an electric field to gain a quantitative measure of charge separation distances in high performance PTB7:$PC_{71}BM$ solar cells. We observe distinct absorption spectra for interfacial charge transfer states and spatially separated charge pairs. We find that ~70% of charge pairs get separated by 2 nm or more in <100 fs in optimised blends. This separation occurs from non-relaxed charge transfer state and is driven by very fast electron diffusion or electron delocalisation over several fullerene molecules. The remaining 30% of charge pairs dissociate into free carriers on a picosecond time scale via relaxed charge transfer states and this process involves diffusion and drift of electrons and holes.

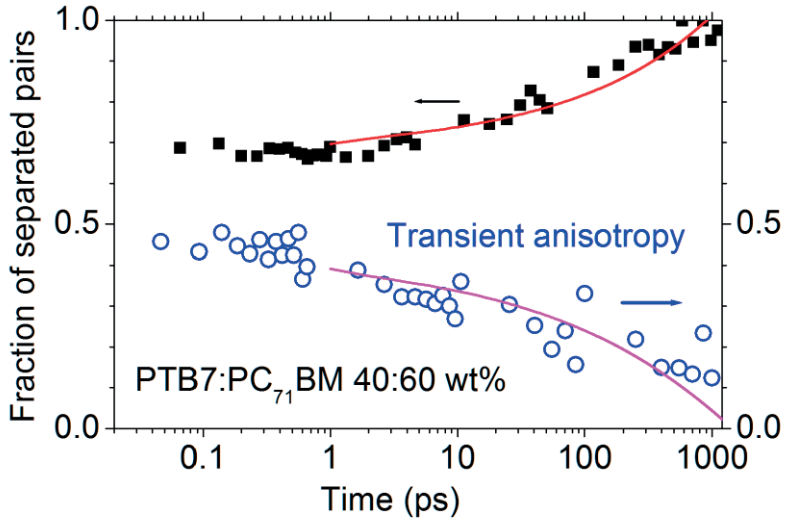

Fig.1. Growth of the fraction of spatially separated charge pairs (solid squares) and depolarisation of ground state bleach of PTB7 (open circles) in optimised photovoltaic blends with fullerene.

Our results show that at least two different charge separation mechanisms occur at organic heterojunctions. Although an ultrafast charge separation via non-relaxed charge transfer states is a dominant mechanism, the dissociation of relaxed charge transfer states can be as efficient as the 'hot' charge separation pathway, provided it has long enough lifetime and there is sufficient carrier mobility to overcome the Coulomb barrier.

Unraveling the Quantum State Mixing of Excitonic and Vibronic Excitations in the Dynamics of Molecular Aggregates

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One possible source of coherent oscillations observed in two-dimensional electronic spectroscopy experiments is the quantum state mixing (QSM) of electronic and vibronic excitations in molecular aggregates. In the present contribution the signatures of Coulomb coupling induced QSM between excitonic and vibronic excitations in the dynamics of a model aggregate are discussed. To this end numerically exact dissipative exciton dynamics calculations applying the hierarchy equations of motion (HEOM) method are performed.

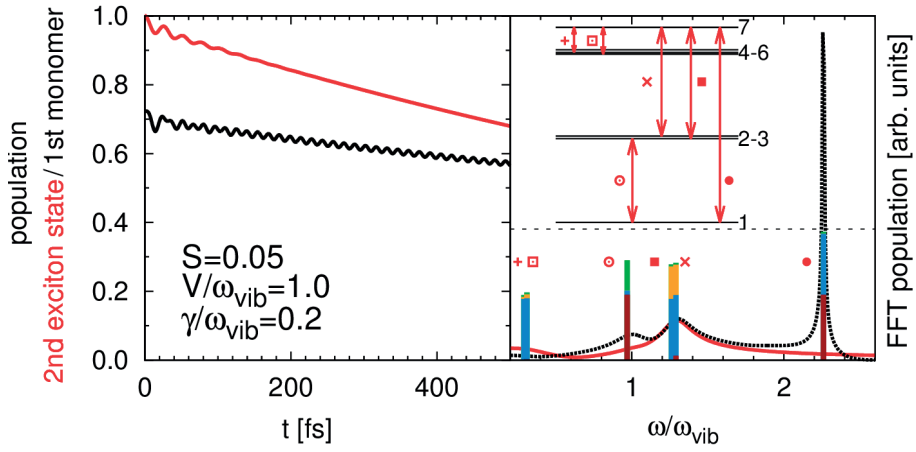

Fig.1. Dynamics of a vibronically weakly coupled hetero-dimer after initial excitation of the higher exciton state (left panel) and corresponding QMS analysis of the oscillatory components (right panel). The colored bars indicate the character of the vibronic-exciton states contributing to the underlying transitions (red/blue: electronic contribution lower/upper state, orange/green vibronic contribution lower/upper state). The vibronic-exciton structure is given by the inset.

A Fourier analysis of the coherent oscillations in the population dynamics after an initial excitation of the highest exciton state is supplemented by exciton-vibronic structure calculations employing direct diagonalization (1). This allows us to unravel the origin of the oscillations and to obtain insights on the general influence of QMS on the dynamics as a function of Coulomb and vibronic coupling strengths (2).

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Title: Energy harvesting in SubPC dyad and triad systems

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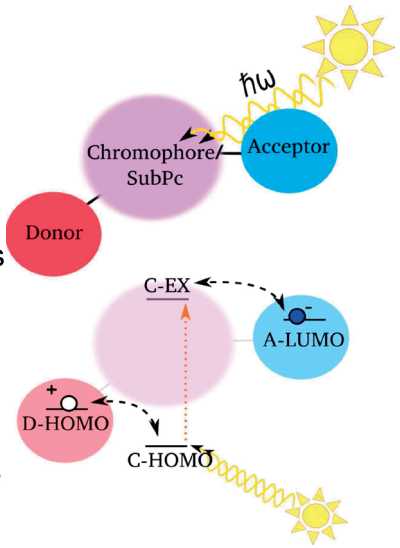
In this work boron subphthalocyanines (SubPcs) functions as chromophores in triads for future use in solar cell applications. The SubPcs have maximum absorption intensities in the visible range of the spectrum. Investigations are performed at DFT/CAM-B3LYP/6-311G(d) level of theory. Calculations show that functionalizing at the boron atom have little effect on the highest intensity/lowest energy absorption peak, but that dimers absorb with twice the intensity at the same wave length as monomers indicating that there is little or no coupling of the moieties in the dimer molecule.
In order to further characterize the systems a simple four level scheme (FLS) for the triads have been developed, where the donor is represented by a single energy level (ground state) the SubPc by two (the ground state and first excited state) and acceptor by one (first excited state).



Based on the computational work the alignment of the energy levels of the systems have been determined, design of a triad system proposed and this will be the focus for future investigations.

Energy couplings of the moieties will be investigated using constrained Density Functional Theory (cDFT), and combination of this data will be used to construct a suitable Hamiltonian in order to model the dynamics of the triads.

The FLS will be placed in a harmonic bath and the time evolution of the system will be studied using the Redfield formalism to model ET reactions at both D-SubPc and SubPc-A interfaces in order to determine the relevant time scale of electron transfer and suggest possible design parameters of candidates for future design.

Effect of HCl etching on carrier recombination processes in InP semiconductor nanowires

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Semiconductor nanowires (NWs) have received intense interest as they have potential for applications in future electronic and optical components.[1] For device applications, NWs with high purity which are uniform in length and diameter are needed. In situ etching by use of HCl has been shown to suppress radial growth and improve morphology and optical properties of InP nanowires (NWs).[2] One would expect that HCl eaching may influence the surface quality and tus charge carrier dynamics in the NW. However, the correlation between HCl etching and carrier recombination processes are not clear.

We have investgated the dynamics of photo-generated charge carriers in a series of InP NWs with varied HCl flux during their growth. Time resolved photo-induced luminescence (TRPL), transient absorption (TA) and time resolved THz (TRTS) measurements have been employed to investigate radiative and non-radiative charge recombination processes and their influence on photoconductivity of NWs. Considering strongly inhomogeneous absorption of light inside the NWs,[3] we can measure carrier recombination processes at the top and at the bottom of the NWs. From TRTS kinetics under excitation at 400 nm (very short penetration depth in NWs), we find that after HCl etching photoconductivity decays slower than without etching, suggesting that the density of the electron traps reduces with increasing HCl etching. The reduced electron trap density can be attributed to improved surface morphology after HCl etching. Comparing TRPL and TRTS, we find that hole trapping dominates PL quenching and that hole trap density is dependent on HCl etching. The lowest hole trap was observed for HCl=0.7 sccm, which has been chosen as the optimal etching via independent experiments. We also see that hole trap density is higher at the top of the NWs than at the bottom in most cases exept for for HCl=0.7 sccm. From TA measurements, we conclude that charges recombine non-radiatively on much longer time scale than PL, which is consistent with the observation of long-lived photoconductivity.

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Table-top time-resolved x-ray spectroscopy

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A dramatic improvement in quantum efficiency during the collection of high resolution x-ray spectra opens the pathway to many new applications and experiments. X-ray spectroscopy with microcalorimeter is very powerful in the energy region from soft to hard x-rays, and it can fill an instrumental gap in lab- and large facility-based absorption and emission spectroscopy and also in time-resolved and other photon starved applications. We have applied this novel approach in lab-based sub-picosecond absorption and emission spectroscopy. Hard x-ray pulses with continuum energy spectrum with sub-picosecond time structure are generated from a laser plasma source based on a water jet target. The liquid-jet target combines a flexible sample environment, easy debris handling with a smooth spectrum free of emission lines and with sufficient flux from a moderately powered 45 fs, 1 kHz laser system in the few mJ class. A compact 160-pixel array of multiplexed superconducting transition-edge microcalorimeters (with up to 16000 counts/s and $E/\Delta E \sim 2000$ at 6 keV) can be positioned close to the sample. This allows an efficient measurement of wide energy range of x-rays beyond any crystal based devices currently installed. X-ray emission spectra have been collected at energies from the soft x-rays range ~ 400 eV (nitrogen Kα) over the tender x-ray range at 2.4 keV (sulphur Kα) to the hard x-ray range at 6.4 keV (iron Kα).
We will discuss how such emerging sources and detection devices can complement existing large scale facilities setups and show our path to table-top time-resolved spectroscopy.

Iron sensitizer converts light to electrons with 92 % yield

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Solar energy conversion in photovoltaics or photocatalysis involves as a first step light-harvesting, or sensitization of a semiconductor or catalyst. For this purpose, rare elements are frequently used as key building blocks, though obviously not ideal for large-scale implementations. Great efforts have been made to replace the widely used ruthenium with more abundant analogs like iron, but without much success due to very short lived excited states of the resulting iron complexes.[1] We have developed an iron-nitrogen heterocyclic carbene sensitizer with a nearly thousand-fold increased excited state lifetime compared to traditional iron polypyridyl complexes (Figure 1).[2] By the use of electron paramagnetic resonance spectroscopy, transient absorption spectroscopy, transient THz spectroscopy, and quantum chemical calculations, we show that the iron complex generates photoelectrons in the conduction band of titanium dioxide with a quantum yield of 92 % from the ^{3}MLCT state (Figure 1). The injection from the ^{1}MLCT state is negligible. These results open up possibilities to develop solar energy converting materials based on abundant elements.

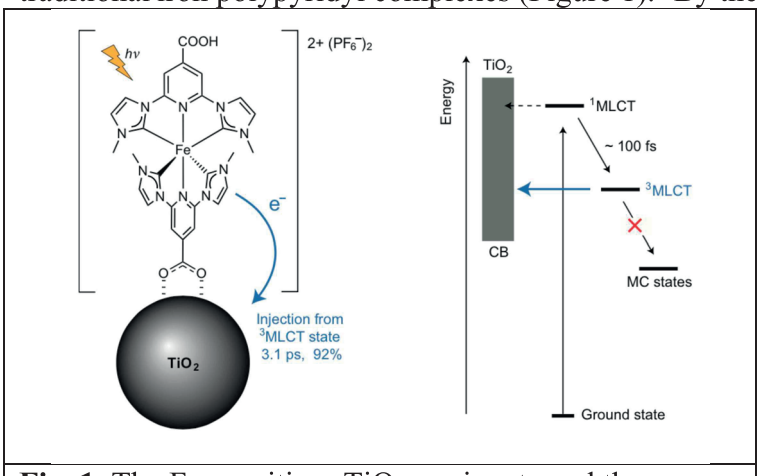

Fig. 1. The Fe-sensitizer-TiO_2-conjugate and the principle behind successful electron injection.[1]

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Efficient Phenothiazine-based Hole Transport Materials for solid-state Dye-sensitized Solar Cells and Perovskite Solar Cells

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The photovoltaic conversion of sunlight into electric energy is an efficient way to use solar energy. Thus, various technologies have been developed in relation to photovoltaics. Among them, solid-state dye-sensitized solar cells (ssDSCs) and perovskite solar cells (PSCs) have been considered as the most promising candidates for next-generation solar cells. In these two types of devices, hole transport materials (HTMs) play an important role to achieve high efficiency. However, as the best one to date [1, 2], the high cost of Spiro-OMeTAD impedes the growth and advancement of highly efficient and cost-effective photovoltaics devices. Therefore, the development of low cost and high-performanced HTMs is highly required [3].
Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. The ring of phenothiazine is nonplanar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers. Thus, phenothiazine has great potential to use as HTMs in many organic electronic devices, such as organic photovoltaic devices (OPVs), organic light-emitting diodes (OLEDs) and film transistors. Herein, we designed three phenothiazine-based HTMs named **L01**, **L02** and **L03**. The syntheses of these phenothiazine-based HTMs are quite simple. The final compounds can be obtained through three steps: one step of bromination reaction and two steps of Buchwald-Hartwig reaction. The low cost of raw materials and facile synthesis of these phenothiazine-based HTMs have great potential to take place Spiro-OMeTAD for application in ssDSCs and PSCs.

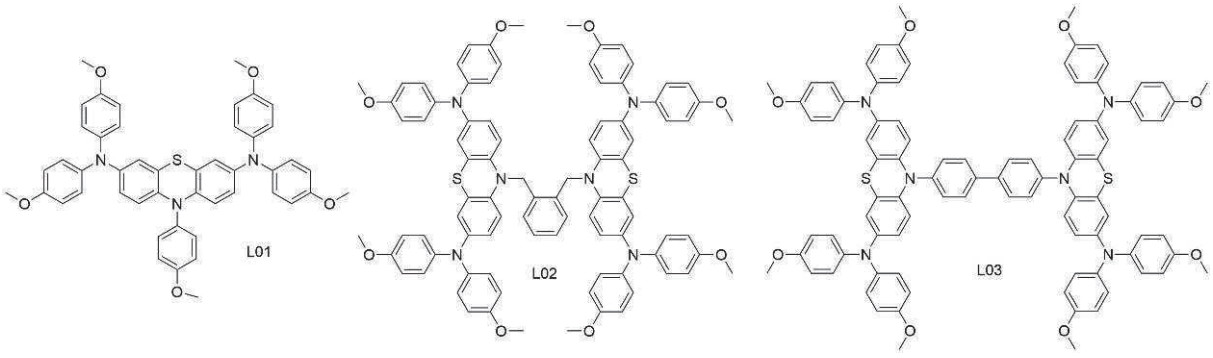

Fig. 1 The structure of L01, L02 and L03.

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Ultrafast molecular dynamics explored by three-pulse transient absorption spectroscopy

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Transient absorption spectroscopy has become a standard technique used for exploring ultrafast dynamics of molecular systems. However, the interpretation of transient absorption results is often problematic due to overlapping spectral bands containing contribution from different photoinduced pathways. In the past 15 years, multi-pulse transient absorption spectroscopy was developed and used to address complex issues regarding the ultrafast dynamics in pigment protein complexes. In this contribution we present three applications. Firstly, the technique is used to investigate the influence of mutations on the proton transfer in Green Fluorescent Protein (GFP). The results of pump-dump-probe experiments are compared between the wild-type GFP and its mutant H148D to draw conclusions about the influence of hydrogen bonds on the excited- and ground state proton transfer. A tentative model involving structural dynamics of the protein coupled to proton transfer pathway is proposed. Second application demonstrates the investigation of excitation energy transfer dependence on the state of acceptor molecule (ground state versus excited state). As model systems, peridinin-chlorophyll-protein (PCP) and caroteno-zinc-phtalocyanine dyad are selected and studied (1). Finally, the relationship between intramolecular charge transfer state and S1 state of peridinin in PCP and their energy transfer properties to chlorophyll are presented.

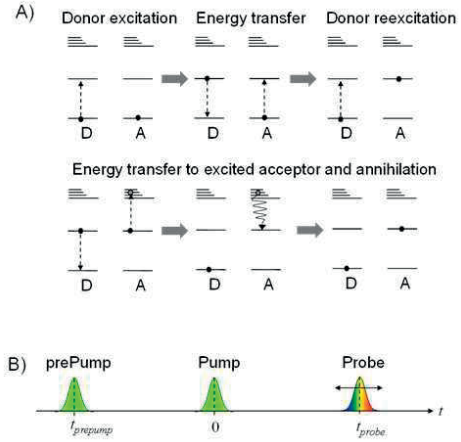

Fig.1. A: Comparison of excitatation energy transfer to an excted and ground state acceptor. B: pulse sequence employed to detect the difference between the two cases.

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Femtosecond Pulse Shaping for Coherent Two-Dimensional Nanoscopy

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Fourier Transform pulse shaping is a versatile tool that enables the generation of ultrashort laser pulses with nearly arbitrary temporal shapes [1]. Among others, the technique is of use in ultrafast spectroscopy experiments where it can be employed for dispersion control and pulse sequence generation [2, 3]. Here, a pulse shaper designed for simultaneous phase and amplitude shaping of femtosecond laser pulses in the visible and near-infrared spectral range is presented. The setup is based on a liquid crystal spatial light modulator (LC-SLM) and uses a prism to spatially separate the spectral components of the input pulses to allow for a high throughput over a large bandwidth.

For accurate pulse shaping a careful calibration of the setup is required. Procedures for determining the pixel-to-wavelength and the wavelength dependent voltage-to-phase mapping of the LC-SLM were developed and are presented. The phase can be retrieved from an *in situ* measurement of the intensity modulation of the pulse shaper using an iterative optimisation algorithm. To validate the calibration results, the pulse shaper was used to arbitrarily shape the spectral amplitude of near-infrared laser pulses. Within the limitations of the pulse shaper, good agreement between measured and desired spectral shape was found, confirming the validity of our calibration procedure. Moreover, dispersion compensation could be successfully demonstrated.

This work provides a platform for pulse-shaper-assisted ultrafast spectroscopy and nanoscopy [4] experiments.

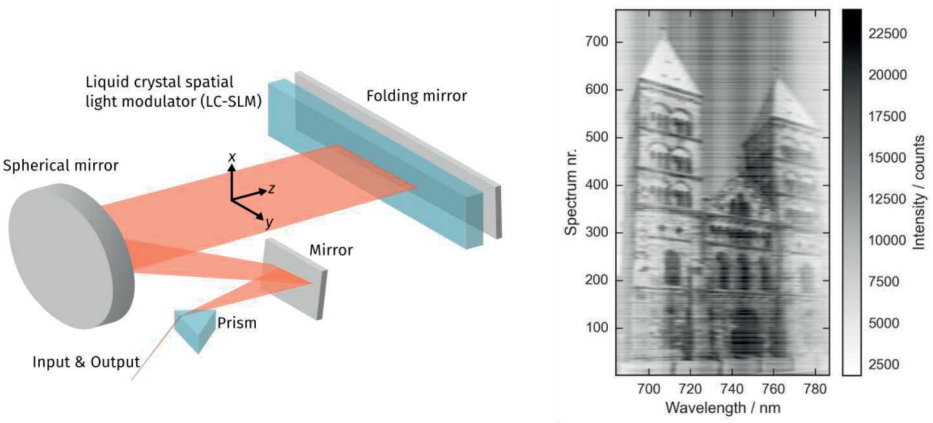

Fig.1. **Left**: Schematic diagram of the pulse shaping setup. **Right**: Example of amplitude shaping (every horizontal line represents a single shaped spectrum)

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Photoisomerization of symmetric polymethine dyes studied by pump-dump-probe spectroscopy

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Despite several decades of investigation, the photoisomerization mechanisms and the structures of photoisomers of polymethine dyes remain elusive. We aimed to address the doubtful issues of photoisomerization with a pump-dump-probe (PDP) study, which, to our knowledge, was not performed on polymethine dyes earlier.

The formation of photoisomers was investigated by depleting the excited state of the dye molecules with a dump pulse, which was tuned to interact with stimulated emission (SE) band. As a result, relaxation of the excited state proceeds via "shortcut".

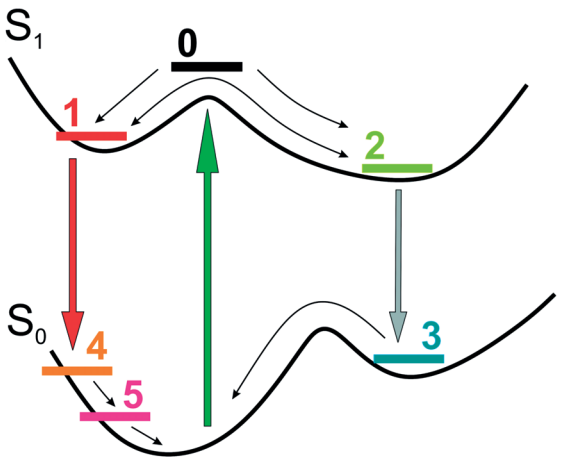

Fig.1. Connectivity scheme used to fit PP and PDP data: green arrow denotes pump, grey arrow – radiationless relaxation, while dump / fluorescence pathway is shown with red arrow.

Two compounds were investigated: one with a very long, nanosecond lifetime of the photoisomers, while the lifetime of the second compound is very short, on the order of several picoseconds (*1*). The presence of the emissive and non-emissive ("dark") states in the excited state manifold of the symmetric polymethine dyes was demonstrated for the first time. Target analysis (Fig. 1) of the transient data suggested the scheme of photoevolution. For both compounds, the "dark" state is the channel of the ground state photoisomer formation, while the emissive state relaxes back to the original ground state.

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Characterization of a Trinuclear Ruthenium Intermediate in Catalytic Water Oxidation by Ru(bda)(pic)$_2$ in Neutral Media

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The oxidation of water is of significant importance to solar energy conversion. In particular, the ability of Ru(bda)(pic)$_2$ (**1**, H_2bda = 2,2′-bipyridine-6,6′-dicarboxylic acid; pic = 4-picoline) and its derivatives towards catalytic water oxidation has been intensively studied by several research groups including us.[1,2] With $Ce(NH_4)_2(NO_3)_6$) as a sacrificial chemical oxidant in acidic media, high initial turnover freqencies (TOF_i) up to 1000 s^{-1} were documented, where a seven-coordinate Ru^{IV}-OH species was characterized by X-ray crystallography as the key intermediate in catalytic cycle.

Herein, a Ru^{III}-O-Ru^{IV}-O-Ru^{III} type trinuclear intermediate [Ru^{III}(bda)(pic)$_2$-O-Ru^{IV}(pic)$_2$(OH_2)(CH_3CN)-O-Ru^{III}(bda)(pic)$_2$]PF_6 (**2**) was crystallographically characterized in water oxidation by Ru(bda)(pic)$_2$ under neutral conditions. The formation of ruthenium trimer due to the comproportionation of Ru^{IV}=O and Ru^{II}-OH_2 was fully confirmed by chemical, electrochemical and photochemical methods. Since the oxidation of trimer leads to catalyst decomposition, the photocatalytic water oxidation activity was rationally improved by lowering pH, which is an efficient way to hinder the formation of trimer.

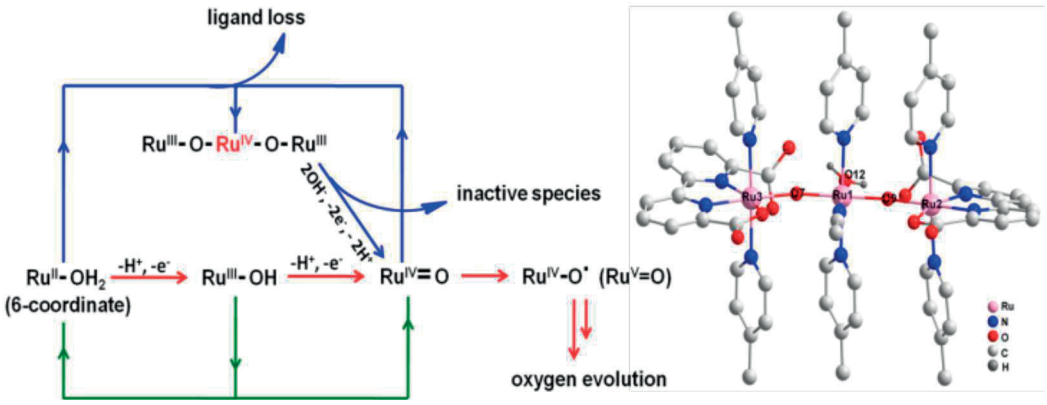

Fig.1. Proposed water oxidation mechanism for complex **1** under neutral conditions and X-ray crystal structure of the cation of complex **2**.

In summary, two important findings were made in this study. First, we have successfully isolated and characterized a high-valent intermediate for Ru(bda)(pic)$_2$-catalytzed water oxidation under neutral conditions. The formation of mixed-valence ruthenium trimer **2** by the comproportionation of Ru^{IV}=O and Ru^{II}-OH_2 is evidenced by chemical, electrochemical and photochemical methods.

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Second Generation of Diketopyrrolopyrrole Dyes for NiO-Based Dye-Sensitized Solar Cells

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In this study four new diketopyrrolopyrrole (DPP) sensitizers (*1*), with a dicarboxylated triphenylamine anchoring group for attachment to NiO, were prepared and their electronic absorption, emission and electrochemical properties were recorded. The nature of the electronic excited-states was investigated with first principle tools. The photovoltaic performances of these new dyes were characterized in NiO based dye-sensitized solar cells (DSCs) with the classical iodide/triiodide and cobalt$^{II/III}$-polypyridine electrolytes. Laser spectroscopy on dye/NiO/electrolyte films gave evidence for ultrafast hole injection into NiO (0.2-10 ps time scales). For the dyes with an appended naphtalenediimide (NDI) acceptor unit, ultrafast electron transfer to the NDI dramatically prolonged the lifetime of the charge separated state NiO$^{(+)}$/dye^{-}, from the ps time scale to an average lifetime ≈ 0.25 ms (Fig. 1), which is among the slowest charge recombinations ever reported for dye/NiO systems. This allowed for efficient regeneration by Co^{III}polypyridine electrolytes, which translated into much improved PV-performance compared to the DPP dyes without appended NDI.

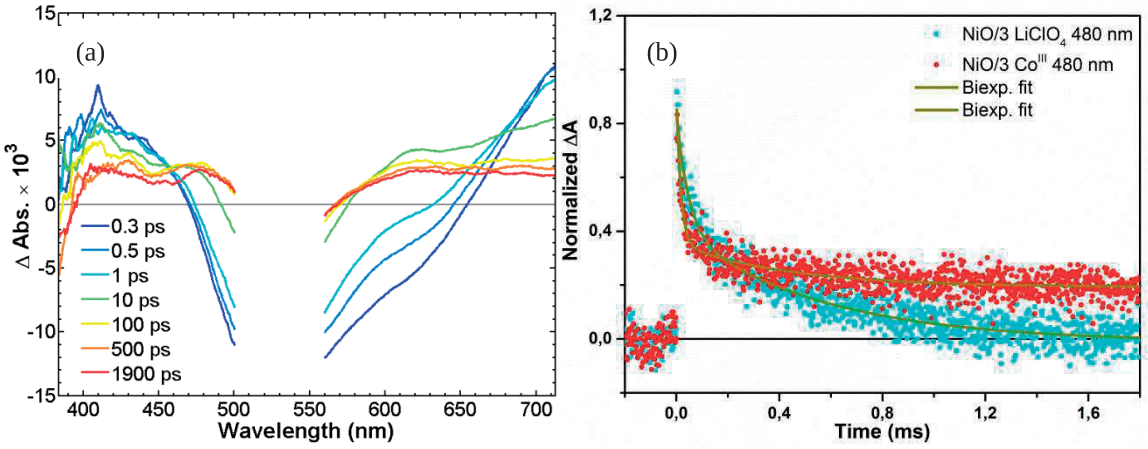

Fig. 1. Femtosecond transient absorption spectra of NiO/3 (a) and nanosecond recombination, re-generation of NiO/3 with or without Co^{III}(dtb)$_3$ electrolyte (excitation at 532 nm) (b) in the presence of 0.1 M $LiClO_4$

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Nature of Emission States and Dynamics of Organometal Halide Perovskites Nanoparticles

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Nowadays, organometal halide perovskites have also shown promise for light emitting diodes (LED) and lasing devices.[1-2] Recently colloidal organometal halide perovskite nanoparticles exhibit high photoluminescence quantum yield compared to the bulk materials.[3-4] In order to utilize the material in opto-electric devices, understanding of such PL enhancement is essential. Here, we investigated the emission states and PL dynamics of colloidal nanoparticles of $CH_3NH_3PbBr_3$ perovskites. By comparing the electronic band gap (characterized by X-ray absorption and photoelectron spectroscopy) to the optical band gap, the exciton binding energy (E_b) in the nanoparticles was then determined to be 5 times higher than for the bulk $CH_3NH_3PbBr_3$. This results in much higher fluorescence quantum yield. We also compared the PL dynamics in these NPs and bulk crystals as shown in Fig. 1. In the bulk, at high excitation concentrations, the fluorescence intensity has quadratic behavior following Saha-Langmuir model due to the non-geminate recombination of charges to form the emissive exciton states.[5] In the nanoparticles, a linear dependence is observed since the excitation concentration per particle is significantly less than one. Even the bulk shows linear emission intensity dependence at lower excitation concentrations. In this case the average excitation spacing becomes larger than the carrier diffusion length suppressing the non-geminate recombination. In addition, the different influence of trap states on the PL dynamics between NPs and the bulk has also been discussed.

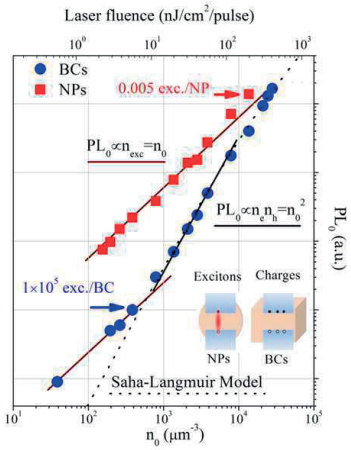

Figure 1. The initial photoluminescence intensity PL_0 in PL decays of NPs and Bulk crystals as a function of excitation intensity n_0.

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Exploitation of compressed sensing in laser spectroscopy

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Laser spectroscopy provides us with valuable information about materials and processes in nature. Current techniques enable us to combine, for instance, measurements of ultrafast dynamics (e.g. of a transient absorption) with deep information about energy states in a material or a high spatial resolution. Such methods are, however, often very complex and require a time-consuming acquisition. In some cases (e.g. photodegrading materials, a wide-range of scanning intervals) the lengthy measurements can even disqualify the method from being used.

A possible solution to the problem lies in applying the so-called compressed sensing (CS).(1) CS is a concept able to highly reduce the acquisition time, while preserving the amount of obtained information - for instance less than 5000 datapoints suffice to reconstruct a simple 1MPix image. The concept employs coding via a random pattern and computational data extraction – see Figure 1.

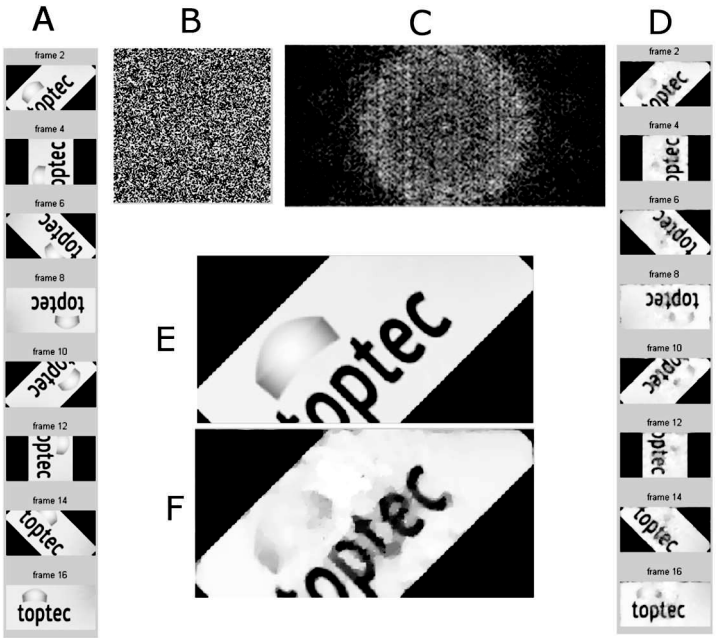

Fig.1. Demonstration of CS reconstruction on artifical data: original set of 16 images (A) encoded via a random mask (B) to a single-shot „CCD image“ (C) is consequently reconstructed into 16 images (D). Comparison of a zoomed original frame (E) and the reconstructed frame (F).

In the contribution we will demonstrate, how the concept can be used in the laser spectroscopy. We will employ a compact, optimized version of a “coded aperture snapshot spectral imaging” (CASSI) experiment to measure evolution of PL emission from Si nanocrystals via a series of single snapshots.

Moreover, we will sketch a novel approach to the CS using a coherent nature of light for creating a coding pattern for CS. This concept has a potential to enable a straightforward application of the CS into a wide range of methods of laser spectroscopy

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