

## ISS 5: Transport and Spectroscopy in Molecular Nanostructures I (CPP, MO, related to SYMN)

Energy transfer in complex molecular aggregates is a very challenging topic with contributions from quite diverse fields certainly including those of molecular and chemical physics. In this section the aggregates range from biological to artificial complexes showing the large range of systems as well as the progress this field has achieved during the last years. The examples range from single molecule experiments over atomistic simulations to complex hybrid aggregates.

Time: Wednesday 14:00–17:00

Location: ZEU 160

ISS 5.1 Wed 14:00 ZEU 160

**Site-specific assembly of DNA-based photonic wires using programmable polyamides** — WU SU<sup>1</sup>, MARKUS SCHUSTER<sup>2</sup>, CLIVE BAGSHAW<sup>3</sup>, ULRICH RANT<sup>2</sup>, and GLENN A. BURLEY<sup>1</sup> — <sup>1</sup>Department of Chemistry, University of Leicester, Leicester, UK — <sup>2</sup>Walter Schottky Institut, TU München, Garching, Germany — <sup>3</sup>Department of Biochemistry, University of Leicester, Leicester, UK

DNA constitutes a unique programmable scaffold for nanotechnological applications where the assembly of functional materials with nanoscale precision is an essential requirement. Of particular interest is the development of nanophotonic sensors and devices where DNA's addressable architecture enables the precise arrangement of fluorophores to produce an optical output. Various approaches for the construction of DNA photonic wires have been investigated; however current methods lack the ability to achieve well-defined and reproducible assemblies with high energy transport efficiency.

Here we show the construction of a site-specific, programmable DNA photonic wire model system by the utilization of fluorophore-tethered-pyrrole-imidazole polyamides (PAs) which inserts a fluorophore at a precise location within a DNA duplex. We demonstrate for the first time the construction of site-directed fluorophore assemblies along a pre-formed DNA duplex and reveal the importance of such control by the demonstration of efficient energy transport over distances in excess of 27 nm.

ISS 5.2 Wed 14:15 ZEU 160

**Single molecule fluorescence-excitation and emission spectroscopy on the same individual light harvesting 2 complexes from *Rps. acidophila* 10050** — RALF KUNZ<sup>1</sup>, KÖU TIMPMANN<sup>2</sup>, ARVI FREIBERG<sup>2</sup>, RICHARD J. COGDELL<sup>3</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimental Physics IV, University of Bayreuth — <sup>2</sup>Institute of Physics, University of Tartu — <sup>3</sup>Institute of Molecular, Cell & Systems Biology College of Medical, Veterinary and Life Sciences, University of Glasgow

Fluorescence-excitation and emission spectra from the same individual light harvesting 2 complexes from *Rps. acidophila* strain 10050 measured at low temperature will be presented. The combination of both spectroscopic techniques provides information about the absorbing and emitting electronic states within the same LH2 complex.

To our surprise we find different types of emission spectra (with/without zero-phonon line) which do not correlate with different types of fluorescence-excitation spectra. The shape of the emission spectra, however, shows a clear correlation with the spectral position.

ISS 5.3 Wed 14:30 ZEU 160

**Photocurrent of a single Photosystem I** — DANIEL GERSTER<sup>1</sup>, SIMONE M. KANIBER<sup>2</sup>, JOHANNES V. BARTH<sup>1</sup>, ALEXANDER W. HOLLEITNER<sup>2</sup>, ITAI CARMELI<sup>3</sup>, and JOACHIM REICHERT<sup>1</sup> — <sup>1</sup>Physik Department E20, TU München, James-Franck Str, D-85748 Garching — <sup>2</sup>Walter Schottky Institut and Physik-Department, TU München, Am Coulombwall, D-85748 Garching — <sup>3</sup>Center for NanoScience and Nanotechnology and School of Chemistry, Tel Aviv University, Israel 69978 Tel Aviv

Photosynthesis in plants and bacteria is driven by photoactive biomolecular complexes. Such photosynthetic reaction centers have evolved approximately 3.5 billion years ago, and they serve as the ultimate source of energy in the biosphere. The photosynthetic process involves an efficient conversion of solar energy to stable chemical energy. Photo-excitation of photosystem I (PS I) causes an electron transfer through a series of redox reactions. We report on the directed photo-current which is generated by a single PS I. The PS I is situated on an Au substrate, and it is electronically contacted by an apertureless scanning near-field optical microscope tip. The tip acts as a light source and counter-electrode at the same time. The PS I is covalently

bound to the electronic circuit via cysteine mutation groups located at both ends of the electron transfer path.

ISS 5.4 Wed 14:45 ZEU 160

**Atomistic modeling of light-harvesting complexes: dissipation, correlation and spectra** — CARSTEN OLBRICH<sup>1</sup>, THOMAS JANSEN<sup>2</sup>, JÖRG LIEBERS<sup>1</sup>, MORTAZA AGHTAR<sup>1</sup>, JOHAN STRÜMPFER<sup>3</sup>, KLAUS SCHULTEN<sup>3</sup>, JASPER KNOESTER<sup>2</sup>, and ULRICH KLEINEKATHÖFER<sup>1</sup> — <sup>1</sup>Jacobs University Bremen, Germany — <sup>2</sup>University of Groningen, Netherlands — <sup>3</sup>University of Illinois, Urbana, USA

The light absorption in light-harvesting complexes is performed by chlorophyll molecules. Recent experimental findings in some of these complexes suggest the existence of long-lived coherences between the individual pigments at low temperatures. In this context the question arises if the bath-induced fluctuations at different chromophores are spatially correlated or not. To this end we performed classical MD simulations and semi-empirical quantum chemistry calculations on some light-harvesting systems [1]. In these investigations at ambient temperatures, only weak correlated movement of the atoms and none for the sites could be observed [2]. Ensemble-averaged wave packet dynamics will be used to study the transfer of energy, i.e., excitons, in light-harvesting systems. On top of this, the same techniques can be employed to determine two-dimensional spectra which can be directly linked to experiment.

[1] C. Olbrich and U. Kleinekathöfer, *J. Phys. Chem. B* 114, 12427(2010).

[2] C. Olbrich, J. Strümpfer, K. Schulten and U. Kleinekathöfer, *J. Phys. Chem. B.* (in press).

ISS 5.5 Wed 15:00 ZEU 160

**Excitons in Molecular Aggregates with Lévy Disorder: Anomalous Localization and Exchange Broadening of Optical Spectra** — ALEXANDER EISFELD<sup>1</sup>, SEBASTIAAN VLAMING<sup>2</sup>, VICTOR MALYSHEV<sup>2</sup>, and JASPER KNOESTER<sup>2</sup> — <sup>1</sup>MPI-PKS Dresden — <sup>2</sup>University of Groningen

We predict the existence of exchange broadening of optical lineshapes in disordered molecular aggregates and a nonuniversal disorder scaling of the localization characteristics of the collective electronic excitations (excitons). These phenomena occur for heavy-tailed Lévy disorder distributions with divergent second moments - distributions that play a role in many branches of physics. Our results sharply contrast with aggregate models commonly analyzed, where the second moment is finite. They bear a relevance for other types of collective excitations as well.

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ISS 5.6 Wed 15:15 ZEU 160

**Size-dependent Excitonic Properties of Perylene Bisimide Aggregates** — STEFFEN WOLTER, FRANZISKA FENNEL, HENNING MARCINIAK, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

The excitonic properties of J-aggregates made from substituted Perylene Bisimides are investigated by stationary and femtosecond spectroscopy. The high quantum yield of 82 % [1] and the recently shown long exciton diffusion length [2] make these aggregates promising candidates for applications like organic solar cells or optoelectronic switches. Here we focus on the excitonic properties in dependence of the aggregate size. Upon heating, a smooth transition from the J-aggregate to the monomer is observed in the absorption spectra. However, the emission shows a distinct minimum of the quantum yield at intermediate temperatures, indicating the existence of a weakly emitting species. Further information on this species is obtained by femtosecond pump probe and fluorescence lifetime measurements. For J-aggregates,

pronounced annihilation is observed, indicating that the excitons are highly mobile. In contrast, almost no remaining annihilation dynamic remains and the fluorescence life time rises abruptly for the weakly emitting state. We discuss the possibility, that the weakly emitting state might be a short H-type aggregate.

[1] Li X.-Q., Zhang X., Ghosh S., Würthner F., *Chem. Eur. J.* 14, p.8074 - p.8078 (2008)

[2] Marciniak H., Li X.-Q., Würthner F., Lochbrunner S., submitted to *J. Phys. Chem.*

## 15 min. break

ISS 5.7 Wed 15:45 ZEU 160

**Demonstration of an organic photonic gate** — ●MARTTI PÄRS<sup>1</sup>, CHRISTIANE HOFMANN<sup>1</sup>, PETER BAUER<sup>2</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We demonstrate the function of an organic photonic gate, that consists of a photochromic switch that is covalently linked to two chromophores. As switch we use dithienylcyclopentene (DCP) that can reversibly be converted by light between two bistable states. As chromophores we employ perylene bisimide, whose fluorescence is monitored as a function of the state of the switch. We present results with respect to the modulation depth of the fluorescence, the quantum yield of the device, and its fatigue resistance.

ISS 5.8 Wed 16:00 ZEU 160

**Spectral shifts and energy transfer in dye-functionalized nanostructures on silicon substrates** — ●THOMAS BAUMGÄRTEL, HARALD GRAAF, and CHRISTIAN VON BORCZYSKOWSKI — Center for Nanostructured Materials and Analytics, Institut für Physik, TU Chemnitz, 09107 Chemnitz, Germany

We use local anodic oxidation (LAO) via atomic force microscopy (AFM) to generate silicon oxide nanostructures with a height of a few nanometers and lateral dimensions below 50 nm on alkyl-terminated silicon. These structures can be selectively functionalized by anchoring optically active materials such as dye molecules or semiconductor nanoparticles via a chemical bottom-up approach. This controlled immobilization of fluorophores on a semiconductor surface with a high positioning accuracy in the nanometer regime is a promising step towards the creation of new types of optical nanoscopic devices and model systems. Especially interesting are the optical properties (e.g. spectral emission, excited state lifetime, transition dipole orientation) of the bound emitters which can show a rather large difference compared to a solution or randomly oriented molecules on a surface. These differences will be discussed as a result of the anchoring mechanism, the close proximity of the emitters to the underlying silicon, intermolecular aggregation and alignment and thus an efficient energy transfer.

ISS 5.9 Wed 16:15 ZEU 160

**Förster Resonant Energy Transfer (FRET) in Orthogonal Chromophores** — ●IGOR PUGLIESI<sup>1</sup>, HEINZ LANGHALS<sup>2</sup>, and EBERHARD RIEDLE<sup>1</sup> — <sup>1</sup>LS BioMolekulare Optik, LMU München — <sup>2</sup>Dept. Chemie, LMU München

FRET has become a process of ubiquitous importance in chemistry and biochemistry. While proximity measurements of light absorbing and fluorescent structures still rely on the basic theory of FRET, recent results from 2D electronic spectroscopy on light harvesting complexes show, that a more refined model is required for an accurate description of this photophysical process [1]. We investigate the very principles of FRET on a set of perylene bisimide dyads by pump-probe spectroscopy, chemical variation and calculations. These dyad undergo transfer with near unit quantum efficiency although the tran-

sition dipole moments of donor and acceptor are in a perfectly orthogonal arrangement to each other in the equilibrium geometry. According to the point dipole approximation used in Förster theory no energy transfer should occur. Experimentally we do, however, observe ultrafast transfer times ranging from 1 ps up to 45 ps. With the transition density cube approach, the change of the spacer both in length and chemical character and temperature variations we demonstrate that energy transfer is enabled through low frequency ground state vibrations, which break the orthogonal arrangement of the transition dipole moments. The dyads presented here therefore are a first example that shows with extreme clarity the decisive role vibrational motion plays in energy transfer processes [2].

[1] Yuan-Chung Cheng and Graham R. Fleming, *Annu. Rev. Phys. Chem.*, 241, 60, 2009.

[2] Heinz Langhals, Andreas J. Esterbauer, Andreas Walter, Eberhard Riedle, and Igor Pugliesi, *J. Am. Chem. Soc.*, 16777, 132, 2010.

ISS 5.10 Wed 16:30 ZEU 160

**Electronic transport through organophosphonate monolayers on silicon/silicon dioxide substrates** — ●ACHYUT BORA<sup>1</sup>, ANSHUMA PATHAK<sup>1</sup>, KUNG-CHING LIAO<sup>2</sup>, ANNA CATTANI-SCHOLZ<sup>3</sup>, GERHARD ABSTREITER<sup>3</sup>, JEFFREY SCHWARTZ<sup>2</sup>, and MARC TORNOW<sup>1</sup> — <sup>1</sup>Institut für Halbleitertechnik, TU Braunschweig, Germany — <sup>2</sup>Department of Chemistry, Princeton University, NJ, USA — <sup>3</sup>Walter Schottky Institut, TU München, Germany

Understanding the electronic transport through layered systems of organic functional layers on semiconductor surfaces is of major importance for future applications in nanoelectronics, photovoltaics and sensors. We have prepared self-assembled monolayers (SAMs) of 9,10-diphenyl-2,6-diphosphono-anthracene and 11-hydroxyundecyl phosphonic acid precursors on highly p-doped silicon surfaces coated with a ~1 nm SiO<sub>2</sub> layer. Contact angle, AFM and ellipsometry evidenced the homogeneity of the formed SAMs, and their thickness was determined to be 0.82 ± 0.07 nm and 1.13 ± 0.09 nm, respectively. We provided large area electrical contacts on top of the SAMs by a hanging Hg drop electrode. The measured I-V characteristics revealed an enhanced conductance of the aromatic vs. the aliphatic compounds, with current densities of the order of 10 A/m<sup>2</sup> and 0.01 A/m<sup>2</sup>, at 0.5 V, respectively. We analyzed the data in terms of non-resonant tunneling through the combined oxide-SAM barrier and found good qualitative agreement up to 0.2 V bias. Preliminary measurements on organized bilayers of anthracene bisphosphonates that were grown using techniques of coordination chemistry will be discussed, too.

ISS 5.11 Wed 16:45 ZEU 160

**Excited states dynamics of two-dimensional donor-acceptor systems** — JULIANE KÖHLER<sup>1</sup>, ●INGO FISCHER<sup>1</sup>, TATJANA QUAST<sup>1</sup>, JOHANNES BUBACK<sup>1</sup>, TOBIAS BRIXNER<sup>1</sup>, and CHRISTOPH LAMBERT<sup>2</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg

Since electron transfer (ET) is one of the fundamental steps in the working principle of optoelectronic devices, the aim of our work is the systematic study of the optically induced ET in donor-acceptor compounds. Our interest lies in the excited states dynamics that is associated with the subsequent back-electron transfer which can be determined by time-resolved transient absorption spectroscopy on a fs- and ps- timescale. Here, we present our recent experimental results on donor-substituted truxenones which are interpreted in the framework of the Marcus theory. As donor we chose the triarylamine because of its low reorganization energy. The truxenone itself is known to be a good acceptor and its C<sub>3h</sub> symmetry allows the substitution of three donor branches. Hence, the ET dimension is extended from one to two. Furthermore we investigated the fluorenone which is the central building block of the acceptor to distinguish their excited state dynamics from the CT state.