

ISS 7: Transport and Spectroscopy in Molecular Nanostructures II (CPP, MO, related to SYMN)

Charge and energy transfer and the respective spectroscopic techniques for molecular nanostructures are the topic of this session. Many of these processes take place on an ultrafast time scale and in a huge variety of different systems ranging from relatively simple molecular to polymeric systems and nanowires bridging the gap between molecular, chemical and solid state physics.

Time: Thursday 10:30–13:00

Location: TOE 317

ISS 7.1 Thu 10:30 TOE 317

Ultrafast electronic dynamics in a polyfluorene based guest-host system — ●HENNING MARCINIAK, MAIK TEICHER, and STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock

Guest-host systems are frequently used for organic solid state lasers to achieve tunability of the emission wavelength and low lasing thresholds. Efficient excitation energy transfer from the host to the guest material and the behavior at high exciton densities are thereby important. We investigate a polyfluorene based guest-host system that shows optically pumped lasing in a distributed feedback structure [1]. Combined analysis of steady state and time resolved spectroscopic studies gives rise to a complex picture of the photoinduced dynamics. Steady state and time resolved fluorescence measurements on the nanosecond timescale show emission signatures from the guest material pointing to efficient excitation transfer from the host to the guest. However, femtosecond pump probe absorption measurements find no signatures of stimulated emission from the guest material but pronounced nonlinear dynamics on the picoseconds timescale. As one quenching mechanism amplified spontaneous emission from the host system is identified, which arises under high excitation densities. However, since the excitation parameters are similar to the nanosecond fluorescence measurements, additional mechanisms have to be taken into account.

[1] T. Riedl, T. Rabe, H.-H. Johannes, W. Kowalsky, J. Wang, T. Weimann, P. Hinze, B. Nehls, T. Farrell, and U. Scherf, *Appl. Phys. Lett.* **88** (2006), 241116.

ISS 7.2 Thu 10:45 TOE 317

Molecular aggregates: handling a complicated vibrational quasi-continuum with non-Markovian quantum state diffusion — ●GERHARD RITSCHEL, JAN RODEN, and ALEXANDER EISFELD — MPI-PKS Dresden

The electronic excitation transfer and the optical processes in molecular aggregates, e.g. light harvesting systems or H-aggregates, are strongly influenced by the coupling to vibrational degrees of freedom – these are internal vibrational modes of the monomers as well as vibrations of the environment. For an adequate theoretical description, that allows us to understand the dynamics of these systems, it is therefore essential to include the vibrations in the calculations.

To this end we apply a new approach, that is based on a non-Markovian quantum state diffusion treatment: a time-dependent stochastic Schrödinger equation for an electronic wave function is solved numerically and the reduced density operator is obtained by averaging over many realizations of the stochastic noise.

This efficient method enables us to calculate spectra and energy transfer dynamics in a non-perturbative way. It is now possible to capture the whole range from coherent dynamics to incoherent diffusion and to investigate the influence of a complicated structured quasi-continuum of vibrations.

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ISS 7.3 Thu 11:00 TOE 317

Time-resolved electron-transfer properties of a low-band-gap neutral mixed-valence polymer — ●FLORIAN KANAL¹, TATJANA QUAST¹, MARTIN KULLMANN¹, STEFAN RUETZEL¹, JOHANNES BUBACK¹, SABINE KEIBER¹, DÖRTE REITZENSTEIN², CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We present measurements of the electron-transfer properties of a polyradical consisting of alternating triarylamine donor and triaryl-methyl radical acceptor moieties. This first polymeric neutral mixed-valence compound is attractive for applications due to its low band gap. It shows an intervalence charge transfer (IVCT) band in the near infrared. The polyradical and a reference monomer were investigated

by liquid-phase fs pump-probe spectroscopy in two different solvents. Excited in the visible spectral range and probed with a whitelight supercontinuum, the transient spectra of the polyradical feature two bands around 550 nm and 650 nm. These bands are assigned to characteristic transitions of the anion and the radical cation, respectively, formed upon optically induced electron transfer. The decay curves exhibit a biexponential decay in the ps time regime. The short-living – solvent dependent – component refers to the direct decay from the IVCT state to the ground state. The long-living – solvent independent – component is tentatively attributed to an equilibrium formation of the IVCT state and a completely charge-separated state.

ISS 7.4 Thu 11:15 TOE 317

Electronic properties of semiconducting polymer nanotubes — ●THOMAS PLOCKE¹, MATTHIAS MÜLLER¹, JANINA MAULTZSCH¹, CHRISTIAN THOMSEN¹, ANDREAS STEFOPOULOS², SOUZANA KOURKOULI³, ELINA SIOKOU³, KOSTAS PAPAGELIS³, and JOANNIS KALLITSIS^{2,3} — ¹Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — ²Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT), 26504, Patras, Greece — ³University of Patras, 26504, Patras, Greece

Single-walled carbon nanotubes were functionalized with different polymeric quinoline chains using the “grafting from” approach in order to combine the properties of the semiconducting polymers with those of the carbon nanotubes [1]. We perform a resonant Raman spectroscopy analysis to study the influence of the functionalization on the electronic properties and the optical transitions of the modified tubes. We observe that the electronic properties of the nanotube derivatives change due to doping effects caused by charge transfer between the tubes and the polymers. Interestingly, our results on different functionalized single-walled carbon nanotubes show frequency shifts for the Raman G-mode in both directions compared to the pristine material. The preparation pathway of the studied samples allows us to distinguish structural from electronic effects caused by the polymer and the metal ion. [1] A. A. Stefoopoulos, S. N. Kourkoulis, E. Siokou, K. Papagelis, M. Müller, T. Plocke, J. Maultzsch, C. Thomsen, J. K. Kallitsis; in preparation (2010).

ISS 7.5 Thu 11:30 TOE 317

Conductance enhancement of InAs/InP heterostructure nanowires by surface assembly of oligo-phenylenevinylene molecular wires — ●MUHAMMED IHAB SCHUKFEH¹, KRISTIAN STORM², ROAR SØNDERGAARD³, ANNA SZWAJCA¹, ALLAN HANSEN¹, PETER HINZE⁴, THOMAS WEIMANN⁴, CLAES THELANDER², FREDERIK C. KREBS³, LARS SAMUELSON², and MARC TORNOW¹ — ¹Institut für Halbleitertechnik, TU Braunschweig — ²Lund University, Solid State Physics, Sweden — ³Risø DTU, Technical University of Denmark — ⁴PTB, Braunschweig

The direct combination of organic molecules with semiconductor nanostructures provides an appealing approach towards possible future nanoelectronic systems. In this context, indium-arsenide is a material of particular interest due to the presence of an electron inversion layer at the surface. We have prepared 50 nm diameter InAs nanowires comprising a 5 nm long InP segment, and contacted them by Ti/Au metallic leads on a planar Si/Si-oxide substrate. Electronic transport measurements at 77 K confirmed the presence of the potential barrier of the InP segment. After investigation of the assembly of 12 nm long, dithiolated oligo-phenylenevinylene (OPV) derivative molecules from solution onto planar InAs surfaces the same recipe was applied to the InAs/InP nanowires, which led to a pronounced, non-linear I-V characteristic, with significantly increased currents of up to 1 μ A at 1 V bias, for a back-gate voltage of 3 V. We attribute this effect to the OPV molecules tethered to the nanowire surface, thereby increasing the surface conductance across the InP barrier.

ISS 7.6 Thu 11:45 TOE 317

Modeling the blinking dynamics of single CdSe/ZnS quantum dots probing their local environment — ●CORNELIUS KRASSELT¹, ROBERT SCHMIDT¹, JÖRG SCHUSTER^{1,2}, and CHRISTIAN VON BORCZYKOWSKI¹ — ¹Institute of Physics and nanoMA (Center for nanostructured Materials and Analytics), Chemnitz University of Technology, Germany — ²now: Fraunhofer Institute ENAS

Fluorescence intermittency, also known as blinking, appears to be a common feature of many different classes of individual emitters like semiconductor quantum dots. Generally it is characterized by inverse power law distributions for both the on- and off- times [1] which are due to trapping and detrapping processes of charges in- and outside the quantum dots, respectively.

This contribution discloses the influences of the local environment surrounding ZnS coated CdSe quantum dots on silicon oxide on their blinking dynamics. We present atypical distributions for the on-time statistics which show deviations from the expected power law behaviour only seen at the beginning of the statistics. These deviations correlate to the local density of hydroxyl groups on silicon oxide but are also measured in polymers such as PS and PVA. Furthermore we are able to resolve the intensity levels of quantum dot time traces via intensity-change-point analysis observing an increasing density of bright intensity levels in case of enhancing on-time deviations accompanied by longer exciton lifetimes. All results are discussed in terms of a model concerning hole trapping processes within the quantum dots.

[1] F. Cichos et al.: COCIS 12 (2007), 272

ISS 7.7 Thu 12:00 TOE 317

Off-time distribution in blinking quantum dots: theoretical investigation — ●PETER REINEKER¹, THOMAS HARTMANN¹, and VLADIMIR YUDSON^{1,2} — ¹Institute of Theoretical Physics, Ulm University, Albert-Einstein-Allee 11, 89069 Ulm, Germany — ²Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142190, Russia

The understanding of blinking quantum dots (QDs) is an open problem since more than a decade. We have investigated the off-time distribution of a semiconductor QD on the basis of an Auger-induced release process of an electron deeply trapped in the QD shell. This release process has not yet been treated in the literature explicitly and starts with the optical generation of an additional electron-hole pair in the off-state of a QD, characterized by a valence band hole in the core and a trapped electron in the shell. This additional pair subsequently recombines and the recombination energy is transferred by an Auger process to the trapped electron. We discuss the efficiency of the release process as compared to the quenching process. For a deep trap occupation density $\sim 1/r_0^6$ (r_0 is the trap distance from the QD center) and a Förster-like release rate, we arrive at an off-time distribution $\sim 1/t_{off}^\alpha$ with $\alpha = 3/2$ in agreement with experimental findings in many QDs.

ISS 7.8 Thu 12:15 TOE 317

Novel Multi-Chromophor Light Absorber Concepts for DSSCs for Efficient Electron Injection — ●ROBERT SCHÜTZ¹, CHRISTIAN STROTHKAEMPER¹, CARLO FASTING², INARA THOMAS^{1,2}, ANDREAS BARTELT¹, THOMAS HANNAPPEL¹, and RAINER EICHBERGER¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ²Institut für Organische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

Dye sensitized solar cells (DSSCs) operate by injecting electrons from the excited state of a light-harvesting dye into the continuum of con-

duction band states of a wide bandgap semiconductor. The light harvesting efficiency of pure organic dyes is limited by a narrow spectral electronic transition. A beneficial broad ground state absorption in the VIS region can be achieved by applying a single molecular dye system with multiple chromophors involving a Förster resonance energy transfer (FRET) mechanism for an efficient electron injection. A model donor acceptor dye system capable for FRET chemically linked to colloidal TiO₂ and ZnO nanorod surfaces was investigated in UHV environment. We used VIS/NIR femtosecond transient absorption spectroscopy and optical pump terahertz probe spectroscopy to study the charge injection dynamics of the antenna system. Different chromophors attached to a novel scaffold/anchor system connecting the organic absorber unit to the metal oxide semiconductor were probed.

ISS 7.9 Thu 12:30 TOE 317

Single molecule diffusion in columnar functionalized mesoporous rods — ●FLORIAN FEIL, VALENTINA CAUDA, JENS MICHAELIS, THOMAS BEIN, and CHRISTOPH BRÄUCHLE — Physikalisches Chemie, LMU München, Germany

Mesoporous silica materials are ideally suited as host-guest systems in nanoscience with applications ranging from molecular sieves, catalysts, nanosensors to drug delivery systems. For all these applications a thorough understanding of the interactions between the mesoporous host system and the guest molecules is vital. Here, we investigated fluorescent dyes as guest molecules acting as molecular probes that were loaded into the channels of mesoporous filaments. The dye AS-TDI was used as a tool to explore the nanoporous channel structure. By sputtering the sample with a very thin layer of gold, which quenches all molecules on the surface, we could show that the molecules were diffusing inside the structure along the columnar channels. Additionally, we could measure the orientation of the TDI molecules, as the channels have such a small diameter that the molecules are not able to rotate freely but have to align parallel to the channels. In a further approach we also succeeded in loading fluorescently labelled DNA into such a mesoporous host system. As mentioned above, we ensured by gold-sputtering that the DNA resides inside the channels and not on the surface of the filaments. Finally, it could be shown by using FRET measurements that the DNA is still intact inside the mesopores. Moreover, we were able to observe DNA diffusion inside the filament channels.

ISS 7.10 Thu 12:45 TOE 317

Characterization of non-covalently modified carbon nanotubes by Raman spectroscopy — ●DARIA KOVALENKO^{1,2}, ANINDYA MAJUMDER², and JÖRG OPITZ^{1,2} — ¹Fraunhofer Institute for Non-Destructive Testing, 01109 Dresden — ²Institute for material science, Dresden University of technology, 01062 Dresden

Raman spectroscopy is a technique which allows getting information about chemical structure of the molecules. Recently it got widely used for examinations of carbon based materials. In this study Raman and UV/VIS spectroscopic techniques were used to characterize the process of modification of carbon nanotubes. Single walled carbon nanotubes were non-covalently bounded using different surfactants. By UV/VIS spectroscopy it was established what surfactants react better with the nanotubes and therefore they become more soluble in water. Raman spectra of the dispersions were obtained. Using them, we got information about the structure of the carbon nanotubes. By the wavenumber of RBM-modes in spectra of the CNT dispersions diameter of the nanotubes were calculated and possible chiralities were proposed. By comparing G- and D-band intensities presence and amount of semi-conducting and metallic carbon nanotubes were determined.