

HL 13: Focus Session: Structural Ordering and Electronic Transport II (jointly with CPP)

Time: Monday 15:00–17:30

Location: ER 270

Invited Talk

HL 13.1 Mon 15:00 ER 270

Single-Molecule Spectroscopy of Conjugated Polymers: Unravelling Chain Conformations from the Bottom Up — ●JOHN LUPTON — Institut für Experimentelle und Angewandte Physik, Universität Regensburg — Department of Physics and Astronomy, University of Utah, Salt Lake City

When considering molecular morphology in the context of plastic electronics, one usually refers to the level of intermolecular order. Yet because of the large molecular weight and the interplay between intrinsically flexible and stiff molecular bonds, intramolecular morphology is crucial in determining the overall macroscopic properties of a material. Single-molecule fluorescence spectroscopy offers a unique approach to quantifying intrachain order and disorder, rigidity and shape, and the respective influence on electronic structure so as to construct a microscopic understanding of a functional material from the bottom up. Examples where the technique has proven particularly successful include polyfluorene, which can display a wide range of intrachain conformations including the extraordinary case of perfect defect-free pi-chains; and in polyhexylthiophene, which exhibits a uniquely broad range of conjugation lengths which can be directly mapped on the single-chain level.

HL 13.2 Mon 15:30 ER 270

Rod-coil transitions in the polymers MEH-PPV and PFO — ●ANNA KÖHLER — Universität Bayreuth, Bayreuth, Germany

In the current work we explore the effect of aggregation of three conjugated polymers, MEH-PPV, PFO and MeLPPP, dissolved in MeTHF. In MEH-PPV, the absorption spectra are a superposition of a broad ("blue") band and a vibrationally well resolved spectrum at lower energies (the "red"-phase) that appears at 190 K and grows at the expense of the blue phase. Obviously there is a temperature-induced transformation from the blue to the red phase. While this is observed in solutions of 5×10^{-6} mol/L, the red-phase is absent in a 10^{-7} mol/L solution. This proves that the formation of the red-phase requires aggregation. A similarly temperature dependent superposition of blue and red features can also be observed for PFO, but upon dilution only the red feature survives. Finally for MeLPPP, the absorption and fluorescence spectra are mono-modal at all temperatures. The results are indicative of a rod-coil transition in the case of MEH-PPV and PFO with a temperature dependence that is characteristic of an order-disorder transition, albeit with different driving forces. In the case of MEH-PPV the planarization of the chain requires chain aggregation. Quantum chemical calculations show the potential for torsional motion of the repeat units is so shallow that the motion of the solvent molecules above the glass temperature is sufficient to prevent chain elongation unless chain pairing occurs. In PFO, however, the tendency towards chain planarization is obviously strong enough to facilitate the elongation of single chains and inter-chain interaction obstructs rather than helps chain elongation.

HL 13.3 Mon 15:45 ER 270

Aggregation in a High Mobility n-type Low Bandgap Copolymer: Implications on Morphology and Charge Transport —

●ROBERT STEYRLEUTHNER¹, MARCEL SCHUBERT¹, IAN HOWARD², CHRISTIAN SCHILLING³, BASTIAN KLAUMÜNZER⁴, ZHIHUA CHEN⁵, PETER SAALFRANK⁴, FREDERIQUE LAQUAI², ANTONIO FACCHETTI⁵, and DIETER NEHER¹ — ¹University of Potsdam, Institute of Physics — ²MPI for Polymer Research, Mainz — ³Nanolytics GmbH, Potsdam — ⁴University of Potsdam, Institute of Chemistry — ⁵Polyera Corporation, Illinois

The prominent copolymer P(NDI2OD-T2) exhibits very high electron OFET mobility of 0.85 cm²/Vs. Recent X-ray studies on P(NDI2OD-T2) revealed an exceptional in-plane order with distinct pi-stacking of the NDI cores (Rivnay et al.) while GIXD and NEXAFS measurements suggested a significant fraction of amorphous content (Schuetfort et al.). By investigating steady state and time dependent UV-Vis absorption/fluorescence spectroscopy on solutions of P(NDI2OD-T2), we identified distinct absorbing species and assigned them to intrachain CT-excitons on disordered chains and to interchain excitations on aggregated chains. These results were confirmed by DFT calculations on individual and stacked chains. Analytical ultracentrifugation showed that aggregation in solution proceeds via the collapse of individual

polymer coils. The analysis of chain aggregation in solution allowed for the quantitative deconvolution of the thin film absorption, yielding the aggregate content. Finally we find that the vertical transport (electron-only devices) is largely affected by the layer crystallinity.

HL 13.4 Mon 16:00 ER 270

Probing Exciton and Charge Dynamics in Low-Bandgap Polymer:Fullerene Blends by NIR Transient Absorption Spectroscopy — IAN HOWARD, FABIAN ETZOLD, CLARE DYER-SMITH, HANNAH MANGOLD, RALF MAUER, MICHAEL MEISTER, and ●FRÉDÉRIC LAQUAI — Max Planck Research Group for Organic Optoelectronics, Max Planck Institute for Polymer Research Mainz, Germany

Low-bandgap polymers are among the most promising donor materials for bulk heterojunction organic solar cells with efficiencies now exceeding 7 %. However, the photophysics of the pristine polymers and the mechanisms of charge generation and recombination in low-bandgap polymer:fullerene blends are still not entirely understood. In this contribution we compare the exciton and charge carrier dynamics of relevant low-bandgap polymers including PCDTBT, PCPDTBT and PTB-type polymers and their photovoltaic blends, which we study by broadband transient absorption (TA) spectroscopy covering a dynamic range from femto- to milliseconds. We present the previously unobserved near-infrared (NIR) spectral range up to 2000 nm, which we observe with our recently developed broadband NIR-TA setup. We show that by detecting the NIR spectral range we are able to distinguish between the spectral features of singlet and triplet excitons as well as charge-transfer states and mobile polarons and that we can study their generation and decay dynamics, which is difficult, if not impossible, by conventional broadband visible transient absorption spectroscopy.

Invited Talk

HL 13.5 Mon 16:15 ER 270

Band dispersion and localized states in organic solids — NOBUO UENO¹ and ●NORBERT KOCH² — ¹Graduate School of Advanced Integration Science, Chiba University, Chiba, Japan — ²Institut f. Physik, Humboldt-Universität zu Berlin, Berlin, Germany

Charge transport in solids is inevitably linked with structural properties. Organic molecular materials are characterized by two hierarchical levels of structure, i.e., the structure of an individual molecule and that of the molecular assembly. As a consequence, both affect the organic solid's electron density of states (DOS) and the mechanisms of charge transport. We give an overview of how photoelectron spectroscopy can be used to study the DOS of organic materials ranging from amorphous thin films to single crystals, and how the sample's structure (including defects) is reflected in localized (gap) states or delocalized dispersing bands. The influence of the molecular chemical structure and the dielectric environment on electron-vibron coupling strength will be discussed. We will address the impact of polymorphism and temperature on the band structure of prototypical organic solids, including tetracene, pentacene, and rubrene.

HL 13.6 Mon 16:45 ER 270

Elucidating excitonic coupling in supramolecular dye nanotubes — ●DORTHE M. EISELE¹, DYLAN H. ARIAS¹, COLBY P. STEINER¹, ROBERT J. SILBEY¹, XIAOFENG FU², DANIELA NICASTRO², KEITH A. NELSON¹, and MOUNGI G. BAWENDI¹ — ¹MIT, USA — ²Brandeis University, USA

Self-assembled molecular nanotubes, in particular those strongly absorbing visible light, are highly promising quasi-1d systems for optoelectronic and light harvesting (LH) applications. A detailed understanding of the energetics, dynamics, and couplings of excitonic states in these nanoscale systems is the key for further development of such applications. We report on a remarkable example of such a system, i.e., well-defined nanotubular aggregates of amphiphilic cyanine dyes [1]. By means of cryogenic electron microscopy and 2d electronic spectroscopy, we show that excitonic interactions in such nanoscale systems are not only highly sensitive to changes within the supramolecular structure, but also to changes in higher ordering [2]. This addresses the fundamental question of what physical properties control the energy transport processes in excitonic nanoscale systems, which are vital for new developments in opto-electronic applications.

[1] D.M. Eisele, *et al.*, Nature Nanotech. 4 (2009); D.M. Eisele, *et al.*, JACS Comm. 132 (2010); D.M. Eisele, C.M. Cone, E.A. Bloemsma, S.M. Vlaming, R.J. Silbey, M.G. Bawendi, J. Knoester, J.P. Rabe, and D.A. Vanden Bout (submitted); [2] D.M. Eisele, D.H. Arias, C.P. Steiner, X. Fu, D. Nicastro, K.A. Nelson, and M.G. Bawendi (to be submitted)

HL 13.7 Mon 17:00 ER 270

Intermolecular torsional motion of a π -aggregated dimer probed by two dimensional spectroscopy — •JOACHIM SEIBT¹ and ALEXANDER EISFELD^{1,2} — ¹Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden — ²Department of Chemistry and Chemical Biology Harvard University, 12 Oxford Street, Cambridge, MA 02138

The energetic splitting of the two exciton states of a molecular dimer depends strongly on the relative orientation of the monomers with respect to each other. The curvature of the corresponding adiabatic potential energy surfaces can lead to torsional motion of the monomers. It has been suggested recently that this torsional motion could provide a possible relaxation mechanism for the upper state which proceeds via a crossing of the two excited state potentials. Another, competing, relaxation mechanism is provided by coupling to the environment, leading to direct exciton relaxation. Here we examine theoretically the combined dynamics of torsional motion and excitonic relaxation for a π -aggregated dimer. Using two dimensional (2D) spectroscopy it is shown how torsional motion through a crossing of the adiabatic excitonic potential surfaces could be distinguished from direct relaxation. For the calculations a mixed quantum/classical approach is

used, where the torsional motion is treated by an Ehrenfest type of equation, while the excitonic dynamics including dephasing and direct relaxation is described by a quantum master equation.

HL 13.8 Mon 17:15 ER 270

Origins of low charge mobility in crystalline acceptor-substituted oligothiophenes — MANUEL SCHRADER¹, ROLAND FITZNER², MORITZ HEIN³, CHRIS ELSCHNER³, BJOERN BAUMEIER¹, MORITZ RIEDE³, KARL LEO³, and •DENIS ANDRIENKO¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Institute of Organic Chemistry II and Advanced Materials, Ulm, Germany — ³Institute of Applied Photophysics, Dresden, Germany

In a small molecule-based organic solar cell, optical absorption in the visible spectrum, needed for efficient photon harvesting, and the relative donor-acceptor level alignment, required for efficient exciton dissociation, are currently achieved by tuning the electron affinity, the ionization potential, and the band gap of the donor material. In dicyanovinyl-substituted oligothiophenes this is realized by covalently binding an electron-withdrawing group (dicyanovinyl) to an electron-donating core (thiophene oligomer). Such an internal donor-acceptor molecular architecture, however, results in large local molecular dipole moments and thus substantial electrostatic energetic disorder, which leads to pronounced Poole-Frenkel behavior and low charge mobilities, even in a crystalline phase. Analyzing charge transport of dicyanovinyl-substituted oligothiophenes, we propose chemical design rules for the donor which offer a compromise between band gap and charge mobility engineering.