

CPP 59: Focus: Static and Dynamic Disorder Phenomena on the Transport in Organic Semiconductors II

Time: Thursday 15:00–18:00

Location: ZEU 222

Invited Talk CPP 59.1 Thu 15:00 ZEU 222

Charge transport modeling in disordered molecular semiconductors: from the molecule to the device — ANDREA MASSE¹, FEILONG LIU¹, PASCAL FRIEDERICH², FRANZ SYMALLA², VELIMIR MEDED², WOLFGANG WENZEL², REINDER COEHOORN¹, and •PETER A. BOBBERT¹ — ¹Department of Applied Physics, Technische Universiteit Eindhoven, Eindhoven, The Netherlands — ²Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany

The modeling of charge transport in disordered organic molecular semiconductors has been hampered up to now by the huge difference between the molecular scale and the device scale at which the transport is studied experimentally. Here, we employ a multi-scale approach in which microscopic information based on ab initio calculations of the morphology, energy disorder, reorganization energies, and charge transfer integrals is stochastically expanded to a scale that allows charge transport calculations at the device scale. We demonstrate the approach for electron and hole transport in a few important molecular semiconductors. For hole-only α -NPD devices, we find a remarkable agreement between predicted and measured temperature-dependent current-voltage and impedance spectroscopy characteristics, without the need to adjust a single parameter. We study the effects of spatial energy correlations and superexchange on charge transport and find that the latter can significantly increase the conductance of host-guest systems used in the emission layers of organic light-emitting diodes.

Invited Talk CPP 59.2 Thu 15:30 ZEU 222

Charge transport in high mobility molecular semiconductors — •HENNING SIRRINGHAUS — Cavendish Laboratory, University of Cambridge, Cambridge, UK

Over recent years there has been tremendous progress in developing low-temperature processible organic semiconductors that provide high charge carrier mobilities for both n-type and p-type device operation, good operational stability and other functionalities such as efficient electroluminescence, sensing or memory functions for a variety of applications. Here we are interested in understanding the charge transport physics of high mobility conjugated polymers and molecular single crystals and the relationship between molecular structure, solid-state microstructure and charge transport. In this presentation we will present our current understanding of the key factors that govern the transport physics and carrier mobilities of these materials.

CPP 59.3 Thu 16:00 ZEU 222

Theory of Thermalization and Recombination in Organic Disordered Semiconductors — •ANDREAS HOFACKER¹, DIETER NEHER², KOEN VANDEWAL¹, and KARL LEO¹ — ¹Dresden Integrated Center for Applied Physics and Photonic Materials, Dresden University of Technology, D-01069 Dresden — ²Institute of Physics and Astronomy, University of Potsdam, D-14469 Potsdam

Charge carrier recombination in organic disordered semiconductors is strongly influenced by thermalization of charge carriers in the density of states (DOS). Measurements of recombination dynamics, conducted under transient or steady-state conditions, can easily be misinterpreted when a detailed understanding of the interplay of thermalization and recombination is missing. To enable adequate measurement analysis, we solve the multiple-trapping problem for recombining charge carriers and analyze it in the transient and steady excitation paradigm for different DOS distributions.

We show that recombination rates measured after pulsed excitation are inherently time-dependent, since recombination gradually slows down as carriers relax in the DOS. When measuring the recombination order after pulsed excitation, this leads to an apparent high-order recombination at short times. As times goes on, the recombination order approaches an asymptotic value. For the Gaussian and the exponential DOS distributions, this asymptotic value equals the recombination order of the equilibrated system under steady excitation. For a more general DOS distribution, the recombination order can also depend on the carrier density, under both transient and steady-state conditions.

CPP 59.4 Thu 16:15 ZEU 222

Dispersive Charge Transport and Recombination in Polymer Solar Cells — •JOHN LOVE and DIETER NEHER — University of

Potsdam

Charge transport in organic semiconductors has long been known as governed by hopping through a broad distribution of localized electronic states. Yet, the role of charge relaxation and dispersive charge transport in the steady state operation of organic solar cells, remains highly debated. Here we address this question, of how thermalization determines the dynamics of charge transport and non-geminate recombination, in the TQ1:PCBM system. Via time delayed collection field, a state-of-the-art dynamic charge extraction technique, we are able to experimentally follow the rate of recombination from nanoseconds to microseconds inside of a working device. We show that the recombination indeed shows a pronounced slowing over time, experimentally validating results of previously published Monte Carlo simulations.[1] The steady state recombination rate at open circuit voltage matches well with the nearly fully relaxed charges found at long time scales of the transient experiments suggesting that open circuit, it is relaxed carriers which undergo recombination.

[1] Melianas, A., Pranculis, V., Devizis, A., Gulbinas, V., Ingnas, O. and Kemerink, M. (2014), *Adv. Funct. Mater.*, 24: 4507.

15 min break

CPP 59.5 Thu 16:45 ZEU 222

Identifying Charge Transfer States in Polymer:Fullerene Heterojunctions by Their Emission Polarization Anisotropy — ANDREAS ARNDT¹, MARINA GERHARD², MARTIN KOCH², ULI LEMMER^{1,3}, and •IAN HOWARD^{1,3} — ¹Karlsruhe Institute of Technology (Light Technology Institute), Karlsruhe, Germany — ²Philipps-Universität Marburg, Marburg, Germany — ³Karlsruhe Institute of Technology (Institute of Microstructure Technology), Karlsruhe, Germany

It is well understood that the separation of charge carriers from donor:acceptor heterojunctions in organic photovoltaic blends is significantly affected by the distribution of charge-transfer states present at the disordered material interface. Recombination of charge carriers held in charge-transfer states can be emissive, meaning the emission spectrum of the charge-transfer states reveals information about interfacial disorder. However, the assignment of charge-transfer state emission can be controversial, especially when the offset to low-energy excitonic emission is small. In this contribution, we present the time-resolved photoluminescence (PL) polarization anisotropy of several organic photovoltaic blends. Our results demonstrate that the charge-transfer state emission can be identified with a high degree of certainty by its unique negative polarization anisotropy. The unique negative anisotropy arises due to the significant rotation of the transition dipole moment upon charge-transfer at the donor-acceptor interface.

CPP 59.6 Thu 17:00 ZEU 222

DFT Study on the Intercalation of Fullerenes and AnE-PV Copolymers — •WICHARD J. D. BEENKEN and CHUAN-DING DONG — Technische Universität Ilmenau, Institut für Physik, Germany

Using density functional theory calculations, we studied the order and disorder of poly(p-anthracene-ethynylene)-alt-poly(p-phenylene-vinylene) copolymers (An-E-PV) with two different substitution schemes for straight and branched side-chains [1,2] and their influence on the intercalation with C₆₀. We found that the calculated ordered and intercalated structures are all in good agreement with the experimental XRD data for films made of ternary blends of these two copolymers with PCBM [3]. The conclusions drawn from the calculated crystal structures and the corresponding electronic band structures explain the experimentally observed variations in photocurrent, photoluminescence [3] and electroluminescence yields with the concentration ratio of the two copolymers in the ternary blend with PCBM.

[1] C.-D. Dong, H. Hoppe, and W. J. D. Beenken, *J. Phys. Chem. A* **120**, 3835 (2016); [2] C.-D. Dong and W. J. D. Beenken, *J. Phys. Chem. B* **2016**, **120**, 10854 (2016); [3] C. Kästner *et al. J. Mater. Chem. A* **1**, 3961 (2013).

CPP 59.7 Thu 17:15 ZEU 222

Origin of high energy photoluminescence in poly(3-hexylthiophene) films — •PHILIPP EHRENREICH¹, DANIEL

PROEPPER², STEFAN JORES¹, ALEXANDER BORIS², and LUKAS SCHMIDT-MENDE¹ — ¹Department of Physics, University of Konstanz, POB M 680, Konstanz 78457, Germany — ²Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

A deeper understanding of exciton dynamics in polymer films is crucially important for improving charge generation in organic photovoltaics further. The large number of already existing polymers and unlimited possibilities of designing new materials demands for model systems, to which a comparison is possible. For this purpose, poly(3-hexylthiophene) is commonly used. Nonlinear decay kinetics have been interpreted by means of hot-excitons, torsional relaxation effects or exciton dissociation at amorphous/crystalline interfaces. However, it is often seen that observations vary. This is attributed to structural or energetic differences that depend on processing conditions. Using temperature dependent time-resolved photoluminescence measurements in combination with low temperature ellipsometry, we can show that P3HT is indeed a model system that follows the common diffusion model of excitons. Based on our results we can exclude the existence of hot-exciton emission as well as an impact of torsional relaxation dynamics on exciton decay dynamics.

CPP 59.8 Thu 17:30 ZEU 222

Ambipolar Seebeck coefficients in high-mobility polymers

— •KATHARINA BROCH^{1,2}, DEEPAK VENKATESHVARAN², VINCENT LEMAU³, YOANN OLIVIER³, and HENNING SIRRINGHAUS² — ¹Cavendish Laboratory, University of Cambridge, JJ Thomson Ave, CB3 0HE Cambridge, UK — ²Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany — ³Laboratory for Chemistry of Novel Materials, Université de Mons, 20 Place du Parc, 7000 Mons, Belgium

Ambipolar polymers with high charge carrier mobilities have attracted considerable interest owing to their potential use in state-of-the-art organic electronic devices. For further advances in mobility and device performance, a deeper understanding of the molecular building schemes leading to low energetic disorder and, in turn, high charge carrier mobilities, is vital. It has been shown that the voltage modulated Seebeck coefficient can be an excellent probe of energetic disorder

within unipolar polymer field effect transistors (FETs) [1], but due to experimental challenges a measurement of the Seebeck coefficient of electrons and holes in ambipolar polymers was difficult to achieve. Here, we report the simultaneous measurement of the Seebeck coefficients of both charge carrier species in high mobility polymers based on diketopyrrolopyrrole and discuss the origins of their high performance in FETs combining our experimental findings with numerical simulations of the energetic broadening of the density of states.

[1] D. Venkateshvaran et al., Nature 2014, 515, 384-388

CPP 59.9 Thu 17:45 ZEU 222

Asymmetric bodipy end-capped oligomer: A molecular seesaw as a polarization-to-wavelength converter — •PHILIPP WILHELM¹, JAKOB SCHEDLBAUER¹, FLORIAN HINDERER², SIGURD HÖGER², JAN VOGELSANG¹, and JOHN M. LUPTON¹ — ¹Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany — ²Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany

Excitation energy transfer (EET) plays a crucial role for the properties of organic photovoltaic devices. Unfortunately, the microscopic pathways of EET are hard to monitor. We therefore introduce a model system, which consists of a π -conjugated donor oligomer (emitting in the blue wavelength region with $\lambda_{\text{max}}=450$ nm) and two different acceptor dyes, based on bodipy (boron-dipyrromethene) derivatives and located at each end of the oligomer. One of the bodipy endcap units emits in the green ($\lambda_{\text{max}}=515$ nm) and the other one in the red ($\lambda_{\text{max}}=650$ nm) wavelength region. By using this molecule with two competing EET pathways from the oligomer to the asymmetric endcaps, we can learn whether the excitation energy migrates preferentially to the global minimum (i.e. the red dye) or if EET is non-deterministic. By employing single-molecule spectroscopy we can address the following questions: does the EET pathway differ between individual molecules? Is the EET pathway like a "seesaw", dynamically changing between red and green over time? Finally, we looked into the question whether the EET pathway can be influenced externally by changing the polarization of the excitation laser. Indeed, we find that the model system can act as a single-molecule light polarization to wavelength converter.