

CPP 3: Focus: Structural Ordering and Electronic Transport I (joint focus with HL)

As yet, there is no complete picture describing the influence of morphology on the transport of excitons and charge in organic semiconductors. This lack of understanding is in part due to the very complex and inhomogeneous morphology of these layers. This session aims to discuss the influence of molecular order, especially intramolecular and intermolecular order in crystalline and amorphous regions, on transport in conjugated molecular systems. Among other subjects, different model systems will be compared, ranging from ordered monolayers in UHV to macroscopic single crystals. (Organizers: Günter Reiter, Dieter Neher, Veit Wagner)

Time: Monday 9:30–13:15

Location: ER 270

Invited Talk

CPP 3.1 Mon 9:30 ER 270

Neither crystalline nor amorphous: how charge transport is affected by order in organic semiconductors — ●ALBERTO SALLEO — Stanford University, Stanford, USA

From the fundamental standpoint, organic semiconductors are fascinating as they are neither crystalline nor amorphous and their microstructure plays a central role in governing charge transport. I will show that understanding disorder is the key to determining charge transport mechanism. Using advanced synchrotron-based X-ray characterization techniques we are able to define and measure structural order at different length-scales. We are particularly interested in cumulative disorder (paracrystallinity), where the lattice parameter takes on a Gaussian distribution about its mean value. The disorder parameter g allows us to rank materials quantitatively on a continuous scale, from a perfectly crystalline material ($g < 1\%$) to an amorphous one ($g > 10\%$). Using disorder as a ranking parameter, I will discuss the differences in transport between small molecule and polymer films as well as their respective inherent limitations and bottlenecks. This work may help devising design rules for new materials with desirable transport properties for polarons and excitons.

CPP 3.2 Mon 10:00 ER 270

Influence of Alkyl Side Chain Length on the Self-organization of RT and Low Temperature Cast Poly(3-alkylthiophene) Thin Films — ●SHABI THANKARAJ SALAMMAL¹, SOUREN GRIGORIAN¹, ULLRICH PIETSCH¹, MARTIN BRINKMANN², NAVAPHUN KAYUNKID², NILS KOENEN³, and ULLRICH SCHERF³ — ¹University of Siegen — ²CNRS, Strasbourg — ³University of Wuppertal

An enhancement of in-plane stacking of poly(3-alkylthiophene)s (P3ATs) with decrease of alkyl side chain length has been thoroughly analyzed using X-ray and electron diffraction (ED) technique. Thin films of poly(3-pentylthiophene), poly(3-hexylthiophene), poly(3-heptylthiophene), and poly(3-octylthiophene) (P3OT) were cast at 23°C (RT) and low (-30°C) temperature. Thin films prepared using the lowest concentration (1mg/14ml) envisages that the P3OT crystallites can provide highly edge-on oriented and bigger crystallites by casting at low temperature. The X-ray and electron diffraction patterns collected for the same films shows the poor in-plane ordering of P3AT crystallites as the side chain length increases due to the augment in steric hindrance between the alkyl side chains. It subsequently reduces the photoluminescence (PL) efficiency as well as the field effect mobility of organic field effect transistors. The reduction in cast temperature together with the reduction of alkyl side chain length is resulting three distinct PL peaks with defined linewidths. The absence of face-on oriented crystallites while casting at -30°C can be explained by the prolongation of growth time caused by the reduced evaporation of solvent (Chloroform).

CPP 3.3 Mon 10:15 ER 270

Determination of the Crystallinity of Semicrystalline Poly(3-hexyl thiophene) by Means of Wide Angle X-Ray Scattering — ●JENS BALKO¹, RUTH LOHWASSER², MICHAEL SOMMER³, MUKUNDAN THELAKKAT², and THOMAS THURN-ALBRECHT¹ — ¹Institute of Physics, Martin-Luther-University Halle-Wittenberg, 06120 Halle — ²Applied Functional Materials, Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth — ³Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge

Poly(3-hexyl thiophene) (P3HT) is a common polymer semiconductor, often used as material or component in organic field effect transistors or solar cells. The crystallinity of this semicrystalline material is among other parameters governing the electronic mobility. However, at

present there is no routine method available to determine an absolute value for the crystallinity, and the values given in the literature e.g. for the enthalpy of melting vary by a factor of three. Wide Angle X-Ray Scattering (WAXS) probes the crystals as well the amorphous parts of the sample and there exists an established procedure to measure the crystallinity (RULAND, 1961) based on scattering data. The result is used for a reliable calibration of the melting enthalpy that can serve as a reference value for more convenient calorimetric techniques. We compare the crystallinity for a number of chemically well-defined samples, with different molecular weight and a typical commercial sample with broad molecular weight distribution. In addition, for some selected samples we study the influence of temperature on crystallinity.

CPP 3.4 Mon 10:30 ER 270

Formation of Single Crystals of Conjugated Polymers — ●KHOSROW RAHIMI¹, IOAN BOTIZ^{1,2}, NATALIE STINGELIN^{2,3}, and GÜNTHER REITER^{1,2} — ¹Institute of Physics, University of Freiburg — ²Freiburg Research Institute for Advanced Studies (FRIAS) — ³Imperial College London

In order to improve optoelectronic properties of conjugated polymers, a profound understanding of the excitonic and electronic transport with respect to structure is crucial. By gaining a precise control over both molecular conformations and morphology we aim to obtain a correlation between orders at a macromolecular level to charge transport properties. The best controlled system for such a study is a single crystal which is free of grain boundaries and molecular disorder/defects.

Here, we report the preparation and structural properties of Poly(3-hexylthiophene) single-crystal grown by crystallization in dilute solutions. By employing a self-seeding approach, we were able to circumvent the nucleation process. To this end, we first dissolved all but a few small thermodynamically stable crystals, which then act as nuclei (seed crystals) for the subsequent crystallization step at higher polymer concentrations or at lower temperatures. This approach extends the accessible range for crystallization to lower degrees of supersaturation or supercooling. Using such conditions, we could control crystal size in all three dimensions as well as aspect ratio.

CPP 3.5 Mon 10:45 ER 270

Developing hybrid simulation schemes for mesoscale modeling of morphologies in organic semiconductors — ●KOSTAS DAOULAS^{1,2}, VICTOR RUEHLE^{1,3}, and KURT KREMER¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Innovation Lab GmbH, Heidelberg, Germany — ³Department of Chemistry, University of Cambridge, United Kingdom

Hybrid simulations use a particle-based description while defining some interactions via collective variables. These degrees of freedom are soft; thus significant speedups of simulations are possible and large systems can be addressed. However, this softness of interactions poses challenges in modeling organic semiconductors where the local liquid structuring (e.g. pi-pi stacking) affects the mesoscale properties. As a first step in developing hybrid approaches incorporating this interplay, we consider here Monte Carlo simulations of homopolymer melts with nematic liquid-crystalline (LC) behavior. The polymers are described as discrete worm-like chains, a simple density functional controls the compressibility, and a functional of the local segmental orientation tensor captures the LC ordering. We illustrate that the method can address large systems parameterized according to volumetric and conformational properties representative of semiconductor materials by establishing a rough correspondence with regiorandom P3HT melts. Chain conformations and the effect of the molecular weight on the isotropic-nematic transition are studied. The formation of the nematic phase is addressed within the Rouse-like dynamics realized by the current model. We discuss directions of further methodological developments.

CPP 3.6 Mon 11:00 ER 270

Structure determination beyond crystallinity — •CHRIS ELSCHNER¹, SEBASTIAN RADKE², GIANAURELIO CUNIBERTI², KARL LEO¹, and MORITZ RIEDE¹ — ¹Institut für Angewandte Photophysik (IAPP), TU Dresden, 01069 Dresden, Germany — ²Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany

Organic semiconducting materials allow novel optoelectronic devices, combining the excellent optical properties of organic dyes with semiconductor behavior. Organic Light Emitting Diodes and Organic Solar Cells are successful examples in this field. Many organic materials grow strongly disordered or even amorphous in thin films. To distinguish between crystalline or amorphous thin films, X-ray diffraction measurements can be used. If Bragg reflections are missing, organic films are simply classified as amorphous in literature without any specification. We show that it is possible to extract short range order informations even from amorphous organic layers. Using a special grazing incidence X-ray diffraction method [1] it is possible to measure the diffuse scattering of amorphous DBP organic layers. A structural model of the short range order within a few nm gives insight of the molecular stacking in the amorphous layer. The structural model is used as starting configuration for mobility calculations based on Monte Carlo simulations. Finally, the correlation between short range molecule stacking and charge transport is investigated.

[1] C. Elschner et al. Journal of Applied Crystallography 44, 983-990(2011).

30 min break: Possibility for discussions

Invited Talk

CPP 3.7 Mon 11:45 ER 270

Charge transport and recombination in organic light-emitting diodes — •PAUL BLOM — TNO Holst Centre, Eindhoven, Netherlands

Charge transport and charge recombination are recognized as key ingredients in the performance of polymer light emitting diodes (PLEDs). We observe that in conjugated polymers the electron transport is limited by traps that are Gaussianly distributed in energy within the band gap. Remarkably, we show that the electron trap distribution is identical for a large variety of polymers, hinting at a common origin for electron traps. Photogenerated current measurements on PLED device structures reveal that next to the known Langevin recombination also trap-assisted recombination is an important recombination channel in PLEDs. The dependence of the open-circuit voltage on light intensity enables us to determine the strength of this process. Numerical modeling of the current-voltage characteristics incorporating both Langevin and trap-assisted recombination yields a correct and consistent description of the PLED, without the traditional correction of the Langevin pre-factor. At low bias voltage the trap-assisted recombination rate is found to be dominant over the free carrier recombination rate. As a result, we show that the ideality factor in the diffusion regime of a bipolar diode is governed by the recombination of trapped electrons with free holes.

CPP 3.8 Mon 12:15 ER 270

Investigations of charge generation, transport and recombination on organic solar cells based on merocyanines — •STEVEN GRAF¹, VERA STEINMANN¹, NILS KRONENBERG¹, MARTIN LENZE¹, DIRK HERTEL¹, FRANK WÜRTNER², and KLAUS MEERHOLZ¹ — ¹Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Str. 116, 50939 Köln (Germany) — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Organic photovoltaics offer a very promising green energy alternative. Highly efficient organic solar cells can be produced by cost-effective methods such as coating from solution (SOL) or depositing under high vacuum conditions (VAC).

We investigate merocyanines (MC), a class of low-molecular-weight colorants, as donor material in organic solar cells. These molecules are processable via both deposition techniques, showing remarkable power conversion efficiencies (PCE) beyond 4% for SOL- and 6% for VAC-processed devices.

Towards even higher PCEs it is imperative to gain a better understanding of the fundamental processes of charge carrier generation,

transport and recombination in MC solar cells. We carried out a detailed study of these processes using steady-state and time-resolved photoluminescence spectroscopy and current-voltage measurements. The influence of morphology on fundamental processes is elucidated by varying the deposition conditions as well as the fabrication method. The investigations are supported by temperature- and electric-field-dependent studies of charge recombination and transport.

CPP 3.9 Mon 12:30 ER 270

Morphology triggered impact of charge carrier recombination on the current-voltage response of organic solar cells — •ALEXANDER FOERTIG¹, MARKUS GLUECKER¹, ALEXANDER WAGENPFAHL¹, CARSTEN DEIBEL¹, and VLADIMIR DYAKONOV^{1,2} — ¹Experimental Physics VI, Julius-Maximilians-University of Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Bavarian Centre for Applied Energy Research (ZAE Bayern e.V.), Am Hubland, 97074 Würzburg, Germany

In view of a commercialization the efficiency of organic solar cells still has to be improved. Therefore a proper understanding of the fundamental physical processes is required. The non-geminate loss mechanisms of photo-generated charges in polymer:fullerene bulk heterojunction solar cells are studied using the complementary measurement techniques charge extraction (CE), transient photovoltage (TPV) and transient photocurrent (TPC). From voltage dependent charge carrier densities $n(V)$ a loss current $j_{loss}(V)$ can be determined. For systems predominately based on a voltage independent charge photo-generation this analysis successfully allows to reconstruct the measured I/V response. Devices based on the promising copolymer PTB7 blended with PC₇₁BM are used to study the influence of morphology on the recombination dynamics and thus the I/V characteristics. Furthermore we applied macroscopic device simulations to analyse the influence of the spatial distribution of charges in the active layer which can not be accounted for in the experiment.

CPP 3.10 Mon 12:45 ER 270

Temperature and carrier concentration dependent analysis of charge transport in Poly (3-hexylthiophene) based organic field effect transistors — •HIPPOLYTE HIRWA and VEIT WAGNER — School of Engineering and Science Jacobs University Bremen Campus 1, D-28759 Bremen (Germany)

A crucial step of organic electronics towards applications is the understanding and exploiting of their charge transport mechanisms. Several models have been previously developed in order to explain the behavior of organic semiconductors. These proposed models (e.g. Vissenberg Matters model, multiple trapping and release model and Neldel Meyer rule) try to include effects like temperature dependence, charge carrier concentration dependence and field dependence. However, these models can not fully explain our experimental data obtained on P3HT based organic field effect transistors manufactured on flexible PET foils. The Neldel Meyer rule hardly showed agreement with our experimental data. The Vissenberg and Matters model and the multiple trapping and release model showed a good agreement but only over a limited temperature range. For temperatures below 170K an additional transport mechanism is observed which is explained by a modification of the Vissenberg and Matters model.

CPP 3.11 Mon 13:00 ER 270

Morphology controlled charge transport in diblock copolymer based solar cells — •CHETAN RAJ SINGH¹, RUTH LOHWASSER², OLESIA SYNOOKA¹, MUKUNDAN THELAKKAT², GERHARD GOBSCH¹, and HARALD HOPPE¹ — ¹Institute of Physics, TU Ilmenau, Germany — ²Applied Functional Polymers, University of Bayreuth, Germany

The block copolymers as an active material have been sought after in solar cells to realize scalable and morphologically stable polymer solar cells. We report here the charge carrier mobilities of holes and electrons in the studied diblock copolymer (P3HT-b-PPerAcr) and in its constituting homopolymers, P3HT and PPerAcr. We discuss the effects of charge carrier mobility imbalance and its consequence on solar cell properties. In the study, the morphology of the diblock copolymer is altered by blending donor component and subsequent thermal treatments which have given rise to up to two orders of magnitude increase in charge carrier mobilities. Furthermore, the influence of morphology and achieved charge carrier mobility balance are studied on solar cell devices.