CPP 24: Organic Semiconductors

Time: Wednesday 9:30–13:00 Location: H40

Invited Talk CPP 24.1 Wed 9:30 H40

Factors determining the contact resistance in organic thin-film transistors — Manfred Gruber[1], •Egbert Zojer[2], Ferdinand Schürrer[1], and Karin Zojer[1] — [1]Institute of Theoretical and Computational Physics, Graz University of Technology, A-8010 Graz, Austria — [2]Institute of Solid State Physics, Graz University of Technology, A-8010 Graz, Austria

The contact resistance is known to severely hamper the performance of organic thin-film transistors. This is particular true when dealing with large injection barriers, high mobility organic semiconductors, or short channel lengths. A common assumption is that the primary quantity determining the value of the contact resistance is the injection barrier at the source electrode. Using drift-diffusion based simulations we show that in sharp contrast to this assumption also the actual device geometry (top- vs. bottom contact), the mobility of the used active material as well as the operation condition of the device can change the contact resistance by several orders of magnitude.[1] The final value of the contact resistance arises from a subtle interplay of all these factors as it is crucially determined by local fields and carrier densities. We also find that the dominant mode of injection (thermionic vs. tunneling) is strongly affected by the above parameters and that (in analogy with the findings of Brondijk et al. [2]) the inclusion of barrier shaping fields, mirror charge effects and recombination at the electrode surfaces [3] is essential to obtain qualitatively meaningful results. [1] Adv. Funct. Mater., prov. accepted, [2] Org. El. 13, 1526 (2012); [3] Org. El. 13, 1887 (2012)

CPP 24.2 Wed 10:00 H40

Stochastic modeling of molecular charge transport networks — •Ole Stenzel[1], Bjoern Baumeier[2], Carl Poelking[2], Denis Andrienko[2], and Volker Schmidt[1] — [1]Ulm University, Ulm, Germany — [2]Max Planck Institute for Polymer Research, Mainz, Germany

Theory and simulations have substantially contributed to our understanding of charge and energy transfer processes in amorphous organic semiconductors.[1] In this talk, we present a stochastic network model for charge transport simulations in amorphous organic semiconductors, which generalizes the correlated Gaussian disorder model to more realistic (off-grid) morphologies, where the information on positional disorder (and other properties) are gained by microscopic simulations.[2] The network model is based on tools from stochastic geometry. It includes an iterative dominance-competition model for positioning hopping sites in space, distance-dependent distributions for the vertex connectivity and electronic coupling elements, and a moving-average procedure for spatially correlated site energies. The field dependence of the hole mobility of the amorphous organic semiconductor, tris-(8-hydroxyquinoline)aluminum, which was calculated using the stochastic network model, showed good quantitative agreement with the prediction based on a microscopic approach. The stochastic model can be used to simulate large system sizes in realistic device geometries.

[1] V. Rühle et al., J. Chem. Theory Comput., 2011, 7 (10), 3335-3345

[2] B. Baumeier et al., Phys. Rev. B, 2012, 86, 184202

CPP 24.3 Wed 10:15 H40

The Impact of energetic disorder on the charge transport in organic molecular crystals — •Sebastian Radke, Rafael Gutierrez, and Gianaurelio Cuniberti — Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, 01062 Dresden, Germany

In a theoretical study combining molecular dynamics simulations, quantum-chemical calculations, and Marcus theory-based charge migration simulations, we investigate the electronic structure and the charge transport of three members of a promising class of organic near-infrared absorber materials: aza-BODIPYs, which are partially already successfully used as the donor material in organic solar cells.[1] The local character of the frontier molecular orbitals and their coupling to the intramolecular dynamics significantly influence the size of the total charge carrier mobility and determine whether a material has a higher electron or hole conductance. These effects depend also on the molecular packing and correspondingly on steric effects causing differences in the ratio between the electron and the hole mobility of highly ordered materials. Interestingly, the fluctuations of the transfer integrals can influence both the total value of the charge carrier mobility as well as its anisotropy. This demonstrates that both local and non-local energetic disorder effects have to be considered to formulate design rules for the class of aza-BODIPY derivatives to help to further improve the efficiency of organic solar cells.

[1] T. Mueller et al. Solar Energy Materials & Solar Cells 99, 176-181 (2012).

CPP 24.4 Wed 10:30 H40

A comprehensive picture of p-doping P3HT with the molecular acceptor F_4TCNQ — •Patrick Pingel and Dieter Neher — Institute of Physics and Astronomy, University of Potsdam, D-14476 Potsdam

Molecularly doped semiconducting polymers can exhibit exceptionally high electrical conductivity, making them suitable for use in solution-processed organic circuitries. It has, however, been shown that the density of the created free charges is well below the density of applied dopant molecules, which has been attributed to aggregation of the dopants and/or insufficient charge carrier dissociation. We used optical absorption spectroscopy, surface potential and conductivity measurements to unravel the mechanism leading to reduced doping efficiency in blends of poly(3-hexylthiophene), P3HT, doped with tetrafluorotetracyanoquinodimethane, F_4TCNQ. Within the broad range of doping ratios investigated, we find that almost every F_4TCNQ dopant undergoes full charge transfer with a P3HT donor site. The majority of these charge pairs remains, however, strongly bound and only ca. 5% of the doping-induced holes on P3HT are mobile and contribute to electrical conduction. The conductivity turns from a sublinear increase (i.e., a decrease of mobility) at low-to-moderate doping ratios towards a superlinear increase at high doping ratios. This dependency is quantitatively reproduced applying a numerical mobility model of Arkhipov et al. [Phys. Rev. B 72, 235202 (2005)], which considers the broadening of the energetic landscape for charge transport upon doping by the Coulomb potential of the left-behind F_4TCNQ anions.

CPP 24.5 Wed 10:45 H40

Characteristics of the temperature dependent excitonic transport of organic semiconductors — •A. K. Topczak[1] and J. Pflaum[1,2] — [1]Exp. Phys. VI, University of Würzburg, D-97074 Würzburg — [2]ZAE Bayern, D-97074 Würzburg

The excitonic transport in organic materials is described either by a temperature activated incoherent hopping model (polymers) or by a band-like coherent transport (single crystals) [1]. To gain insights into the respective behavior we performed temperature dependent Photoluminescence (PL) quenching measurements on the excitonic transport of the archetypical material C_{60} and Diindenoperylene (DIP). The morphological thin film structure of these two materials differs substantially. Whereas C_{60} is X-ray amorphous, DIP shows high crystalline order along the direction of exciton transport. By the PL quenching technique we obtained information of the temperature dependence of exciton diffusion and thereby on the related activation energies in correlation to the underlying film morphology. In the case of DIP we observed indication for a temperature independent exciton motion below 80 K and below a critical thickness of 80 nm. Together, this hints at a coherent exciton transport within the single crystalline domains of DIP and which becomes thermally activated if the exciton has to cross grain boundaries within the layer. This result emphasizes the importance of long range crystalline order to achieve maximum exciton harvesting in planar heterojunction photovoltaic cells and thereby to enhance their performance. Financial support by the DFG (project SPP1355). [1] P. Stallinga, Adv. Mater. 23 (2011) 3356-3362

CPP 24.6 Wed 11:00 H40

Unraveling the extraordinary conformational flexibility of poly(3-hexyl thiophene) by single-molecule spectroscopy — •Florian Steiner[1], Jan Vogelsang[1,3], Alex Thiessen[2], Takuji Adachi[1,3], and John Lupton[1,2] — [1]Universität Regensburg — [2]University of Utah — [3]University of Texas at Austin

Poly(3-hexyl thiophene) (P3HT) has been used for many years for organic solar cells and field-effect transistors due to effective intermolecular selforganization in bulk films. It has been shown that the optical properties strongly depend on the processing conditions. Using single-molecule spectroscopic techniques we are able to link the conformation of the P3HT chains embedded in a host matrix with their photophysical properties. We show that the conformation of a single polymer chain can be influenced by the polarity of the environment, which has been identified by measuring the excitation polarization dependence by wide-field fluorescence microscopy. Additionally, by performing confocal microscopy we could relate the conformation to specific fluorescence characteristics: an ordered conformation leads to a large red-shift of the fluorescence emission of more than 100 nm, accompanied by strong photon anti-bunching, longer fluorescence lifetime and a decrease of the fluorescence quantum yield as compared to a disordered conformation. The data clearly exemplifies the large conformational and spectroscopic variability of P3HT at the single molecule level. We propose that the vast unprecedented variability in single-chromophore transition energies actually drives selforganization in the solid, offering a challenge for future materials and device optimization.

15 min. break

CPP 24.7 Wed 11:30 H40

Molecular Ordering and Charge-Transport Properties of Semi-Crystalline Conjugated Polymers via Computer Simulations — •Carl Poelking[1], Eunkyung Cho[2], Alexander Malafeev[3], Viktor Ivanov[3], Kurt Kremer[1], Chad Risko[2], Jean-Luc Bredas[2], and Denis Andrienko[1] — [1]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — [2]Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, USA — [3]Physics Department, Moscow State University, Moscow, Russia

We establish a link between the microscopic ordering, charge-transport parameters and carrier mobilities for semi-crystalline polymeric semiconductors using a computational multiscale approach. As material examples, we investigate poly(bithiophene-alt-thienothiophene) (PBTTT) and the polymorphic poly(3-hexyl-thiophene) (P3HT). We identify the structural origin of the regioregularity effect on mobility as a broadened energetic density of states and resolve how the packing of side chains, ranging from highly crystalline to amorphous, affects dynamics and distributions of site energies and electronic couplings via orthogonal modes of the backbone paracrystallinity. Simulated hole mobilities are in excellent agreement with experimental values for organic field-effect transistors. The results underline that to secure efficient charge transport in conjugated polymers, (i) electronic couplings should present fast dynamics next to high average values, and (ii) backbone paracrystallinity (intimately related with energetic disorder) should be small.

CPP 24.8 Wed 11:45 H40

Triplet state kinetics of anthracen studied by pulsed electron paramagnetic resonance — •Silvia Domingo Köhler, Sebastian Höfel, and Malte Drescher — Universität Konstanz, 78457 Konstanz, Germany

Photoexcited triplet states (total spin S = 1) of anthracen in a glassy toluene matrix were investigated using pulsed UV-laser photoexcitation and pulsed EPR spectroscopy. The optical spin polarization was studied time dependently resulting in the determination of the triplet lifetime and the triplet relaxation rates between the high-field eigenstates. The relative triplet state populations in zero-field and high-field are quantitatively analyzed. The kinetics of the triplet states were measured for different orientations of the molecule.

CPP 24.9 Wed 12:00 H40

Model systems for interchromophoric interactions in conjugated polymer materials — •Thomas Stangl[1], Sebastian Bange[1], Daniela Schmitz[2], Dominik Würsch[1], Sigurd Höger[2], Jan Vogelsang[1], and John M. Lupton[1] — [1]Universität Regensburg, Regensburg, Deutschland — [2]Universität Bonn, Bonn, Deutschland

A set of pi-conjugated oligomer dimers templated in molecular scaffolds is presented as a model system of the interactions between chromophores in conjugated polymers. Single-molecule spectroscopy was used to reveal energy transfer dynamics and electronic aggregation between two oligomers in either parallel conformation with different well-defined distances or oblique-angle geometry. First, it is concluded that the model systems presented here can be used to investigate the impact of H-aggregation as a function of interchromophoric distance by lifetime and single-molecule spectral measurements. Second, the long-term non-equilibrium dynamics of energy transfer within the weakly coupled bichromophoric systems, however, is found to be accessible by studying the linear dichroism in emission at the single-molecule level, revealing reversible switching of the emission between the two oligomers. In bulk polymer films, strong and weak interchromophoric coupling impacts the functionality, e.g. the emission colour and the migration of excitation energy to quenching sites. Realizing the presence and dynamics of such interactions is crucial for understanding limitations in quantum efficiency of larger conjugated polymer materials.

CPP 24.10 Wed 12:15 H40

Probing charge carrier - exciton interactions in Diindenoperyleneby the photoluminescence response of thin film transistors — •N.H. Hansen[1], C. Wunderlich[1], A.K. Topczak[1,2], and J. Pflaum[1,3] — [1]Experimental Physics VI, Julius Maximilians University of Würzburg, 97074 Würzburg — [2]Center for Nanosystems Chemistry, 97074 Würzburg — [3]ZAE Bayern, 97074 Würzburg

Exciton loss mechanisms play a significant role in organic devices such as organic photo-voltaic cells (OPVs) or organic light emitting diodes (OLEDs). We present a novel approach to investigate the interplay between excitons and charge carriers by means of photoluminescence (PL) measurements on organic thin film transistors (OTFT). For this purpose, the organic semiconductor Diindenoperylene was utilized as active OTFT material. The OTFT geometry benefits from a spatially defined zone for the interaction between charges and photo-generated excitons leading to an intensity reduction of the DIP photoluminescence of up to 4.5%. This effect is found to correlate with the accumulated hole carrier density below the threshold voltage and provides access to the non-radiative exciton-hole recombination rate. Taking into account the respective measurement geometry, the estimated recombination rate of about $0.3 \cdot 10^{-10} \frac{cm^3}{s}$ compares sufficiently well with data reported on single crystals [1]. From the similarity of the threshold voltage and the saturation voltage above which the quenching becomes constant, we conclude the quenching process to be preferentially mediated by trapped holes within the DIP accumulation layer. [1] N. Wakayama and D.F. Williams, J. Chem. Phys., 57(4):1770, 1972

CPP 24.11 Wed 12:30 H40

Particularities of Charge Carrier Localization in $(\mathrm{DOEO})_4[\mathrm{HgBr}_4]\cdot\mathrm{TCE}$ Single Crystals — •Alisa Chernenkaya[1,2], Katerina Medjanik[1], Aleksandr Kotov[2], Andrei Gloskovskii[3], Oksana Koplak[2], Eduard Yagubskii[2], Gerd Schönhense[1], and Roman Morgunov[2] — [1]Inst. für Physik, Univ. Mainz, Germany — [2]Inst. of Problems of Chem. Phys., Rus. Acad. of Science, Russia — [3]HASYLAB/DESY, Hamburg, Germany

The combination of classical conductivity measurements with electron spin resonance (ESR) spectroscopy, hard X-ray photoelectron spectroscopy (HAXPES, experiment has been performed at PETRA III (beamline P09)) and near edge X-ray absorption fine structure (NEXAFS) make it possible to characterize electronic processes around the critical temperatures in the organic charge transfer salts. We discuss the example of $(\mathrm{DOEO})_4[\mathrm{HgBr}_4]\cdot\mathrm{TCE}$ that was studied by means of the methods mentioned above [1, 2]. It was found that the charge carrier localization begins at $T = 140$ K and at $T \leq 70$ K there is clear evidence of two types of centers. Electrons in the crystal give different signals below the critical temperatures: there is an additional line in ESR spectra, a sharp jump in the temperature dependence of SQUID data and shifts of core-level positions in the HAXPES spectra.

Funded via DFG (Transregio SFB TR49) and BMBF (05K 12 UM2).

[1] A. Bardin et al., *Coord.Chem.*, 32, 88 (2006)

[2] A. Chernenkaya et al., *Synth.Met.*, submitted

CPP 24.12 Wed 12:45 H40

Organic π-conjugated copolymers as molecular charge-qubits — •Cesar Augusto Mujica Martinez, Peter Nalbach, and Michael Thorwart — I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstraβe 9, 20355 Hamburg, Deutschland

Organic π-conjugated polymers are systems that combine the electronic properties of semiconductors and the mechanical properties of plastics. Similar to their inorganic semiconductor heterostructures counterparts, it is possible to control the spatial degrees of freedom of charge carriers by constructing unimolecular organic heterostructures from π-conjugated block copolymers. We propose a design for molecular charge-qubits based on poly-(p-phenylene) and poly-diacetylene

π-conjugated heterostructures and determine their electronic structure as well as their vibrational active modes. By tuning the length of the constituent oligomers, the tunnel coupling in the charge qubit and its decoherence properties due to molecular vibrations can be chemically engineered. Long coherence times are observed even when the qubit is operated at room temperature. It is found that the molecular vibrational spectrum induces strong non-Markovian electronic effects which support the survival of quantum coherence.