

CPP 16: Organic Electronics and Photovoltaics: Transport of Charges - from Molecules to Devices (joint session with HL, TT)

Time: Tuesday 9:30–13:00

Location: C 130

CPP 16.1 Tue 9:30 C 130

Electronic properties of biphenylene and the biphenylene carbon sheet — ●JOHANN LÜDER, BIPLAB SANYAL, OLLE ERIKSSON, CARLA PUGLIA, and BARBARA BRENA — Department of Physics and Astronomy, Uppsala University, Sweden

Biphenylene ($C_{12}H_8$) is a promising candidate for applications in molecular electronics as well as a building block for two dimensional materials such as the biphenylene carbon (BPC) sheet, a possible alternative for graphene in nanoelectronics. The electronic structure of the gas phase biphenylene molecule is measured by core and valence level spectroscopy and detailed insights are revealed in conjunction with Density Functional Theory calculations. Hybrid functional calculations including the recently proposed OT-RSH functional are compared to GW calculations to provide an accurate theoretical description. Using the band structure obtained from GW calculations, we compute the optical adsorption spectrum by solving the Bethe-Salpeter equation of BPC. Typically for two-dimensional materials, a strong excitonic effect is found and bright and dark excitons are determined.

CPP 16.2 Tue 9:45 C 130

Dimensionality of excitation transport in sol-gel-derived polymeric carbon nitride photocatalysts — ●CHRISTOPH MERSCHJANN^{1,2}, STEFANIE TSCHIERLEI¹, KAMALAKANNAN KAILASAM³, ARNE THOMAS³, DIRK HOLLMANN⁴, and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — ²Freie Universität Berlin, D-14195 Berlin, Germany — ³Leibniz-Institut für Katalyse, D-18059 Rostock, Germany — ⁴Technische Universität Berlin, D-10623 Berlin, Germany

The spectral and temporal development of optically excited states in highly active sol-gel-derived polymeric carbon nitride (SG-CN) photocatalysts is investigated using time-resolved optical spectroscopy. By combining transient absorption results from a femtosecond pump-probe setup and transient photoluminescence using streak-camera investigations, the evolution of a light-emitting species appearing upon UV excitation is obtained. The emission decay reveals a universal power-law behaviour over more than seven decades in time (150 fs to 5 μ s), the main difference between samples being the characteristic decay time in the nanosecond range. This finding is consistently described using a random-walk approach for the diffusive transport of light-induced polaron pairs, including both geminate and bimolecular recombination mechanisms. Thus, important features of the light-induced charge transport, namely the dimensionality and the regime of reasonable carrier mobilities, are deduced.

The validity of the approach is shown via comparison to ESR-based carrier-density measurements and photocatalytic activities.

CPP 16.3 Tue 10:00 C 130

Simulation of Charge Transport in Organic Self-Assembled Monolayers for Applications in Field-Effect Transistors — ●SUSANNE LEITHERER¹, CHRISTOF JÄGER², MARCUS HALIK³, TIM CLARK², and MICHAEL THOSS¹ — ¹Institute for Theoretical Physics, University Erlangen-Nürnberg, Germany — ²Computer-Chemie-Centrum, University Erlangen-Nürnberg, Germany — ³Institute of Polymer Materials, University Erlangen-Nürnberg, Germany

We study charge transport through self-assembled monolayers (SAMs), which are used in field-effect transistors [1], employing a combination of molecular-dynamics simulations, semiempirical electronic structure calculations and Landauer transport theory. In particular, we investigate SAMs consisting of multifunctional molecules, where the active π -system is linked to a flexible insulating alkyl-chain. We find a close relation between the transport characteristics and the structural and electronic properties of the SAM [2]. For selected systems, we analyze pathways for efficient charge transport by examining local currents in the molecular layers. The pathways are compared to those obtained using Metropolis Monte Carlo (MC) path searches. In order to study the time-dependence of the preferred electron paths, we consider snapshots of the system selected at different times of a MD simulation. To further examine the influence of fluctuations on the transport properties, we utilize a time-dependent approach of charge transport using time-dependent nonequilibrium Green's function (NEGF) theory.

- [1] C. Jäger *et al.*, J. Am. Chem. Soc. **135**, 4893 (2013)
 [2] S. Leitherer *et al.*, J. Chem Phys. **140**, 204702 (2014)

CPP 16.4 Tue 10:15 C 130

Quantum Molecular Dynamics Studies of Polymer-based Thermoelectric Materials — ●HÅKAN W. HUGOSSON, AMINA MIRSAKIYEVA, and ANNA DELIN — Department of Materials och Nano Physics, Royal Institute of Technology KTH, Stockholm, Sweden

Using modern quantum molecular dynamics methods (QMD), where all the interactions are calculated from an electronic structure method (here density functional theory - DFT), we study the polymer-based thermoelectric material PEDOT and its charge carrying polarons. QMD simulations are parameter-free and enable a direct and potentially unbiased simulation of chemical and physical events. Since temperature is taken into account a sampling of the conformational space is made, also making simulations less biased upon choices of e.g. initial conditions and chosen reaction coordinates. Among these studies we will focus on the theoretical modeling of the properties and dynamics of polarons and bipolarons in PEDOT-oligomers and crystals and the effect of novel dopants in PEDOT.

Organic polymer-based thermoelectric materials (like PEDOT), unlike presently used inorganic thermoelectric materials composed of hazardous elements with low natural abundance, though presently being less efficient, can be mass-produced at a low cost using safer abundant elements.

CPP 16.5 Tue 10:30 C 130

First-principles based descriptor for intrinsic charge carrier mobility in organic devices — ●CHRISTOPH SCHÖBER, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

In organic electronics charge carrier mobility is a key performance parameter. Due to the complex manufacturing processes of e.g. organic field effect transistors (OFETs) measured mobilities are often heavily affected by the device preparation. This masks the intrinsic materials properties and therewith hampers the decision whether further device optimization for a given organic molecule is worthwhile or not. Within hopping models based e.g. on Marcus theory the intrinsic mobility can be reliably calculated from first principles. Using a perturbative approach to this theory we formulate a descriptor that can be efficiently calculated for a wide range of organic molecules. For this descriptor we obtain good correlations to fully calculated mobilities, as well as to highest-quality experimental data where device preparation uncertainties are minimized. This suggests the descriptor as a useful tool for materials screening and quick assessment of device-related influences in measured mobilities.

CPP 16.6 Tue 10:45 C 130

Effect of Mesoscale Ordering on the Energy Landscape of a Conjugated Polymer — ●CARL POELKING, PATRICK GEMÜNDEN, KURT KREMER, KOSTAS DAOULAS, and DENIS ANDRIENKO — Max Planck Institute for Polymer Research, Mainz, Germany

A multiscale simulation approach is proposed to study the effect of morphology on charge transport properties of polymeric semiconductors, with poly(3-hexylthiophene) as a test case. The method incorporates both long-range conformational disorder and local ordering, and permits reintroduction of atomistic details into large-scale morphologies generated with a coarse-grained simulation approach. Based on the resulting atomistically resolved mesophases, we investigate how the energy landscape and spatial correlations thereof evolve with increasing degree of structural order in partially ordered systems. We show that a shift towards larger conjugation lengths plays a role in the amplification rather than formation of low-energy states, such that decreased energetic disorder rather than a decreased energetic mean characterize energetics in crystalline domains.

CPP 16.7 Tue 11:00 C 130

The role of microstructure on charge transport in semicrystalline polymers — ●RICCARDO DI PIETRO¹, IYAD NASRALLAH², JOSHUA CARPENTER³, LISA KOELLN⁴, LARS THOMSEN⁵, CHRISTOPHER R. MCNEILL⁶, ANTONIO FACCHETTI⁷, HARALD W. ADE³, HEN-

NING SIRRINGHAUS², and DIETER NEHER⁴ — ¹Hitachi Cambridge Laboratory, UK — ²University of Cambridge, UK — ³North Carolina State University, Raleigh, USA — ⁴University of Potsdam, Germany — ⁵Australian Synchrotron, Clayton, Australia — ⁶Monash University, Clayton, Australia — ⁷Polyera Corporation, Skokie, USA

We present a study on charge transport on two widely used semiconducting polymers, P(NDI2OD-T2) and P3HT. Combining field effect transistor characterization and charge accumulation spectroscopy we provide a consistent and unambiguous correlation between the charge density dependence of mobility and the semicrystalline morphology of the polymer film. This new experimental evidence demonstrates that charge transport in semicrystalline polymers cannot be described using any currently available charge transport model such as multiple trap and release or variable range hopping. A new charge transport model is therefore proposed, which explicitly accounts for the presence of both crystalline and amorphous regions within the polymer film and for the coulombic repulsion between charge carriers accumulated within the same crystallite. It finally provides a coherent picture of charge transport that has important general consequences in regimes that are relevant not only for transistors but also diodes and solar cells.

15 min. break.

CPP 16.8 Tue 11:30 C 130

The molecular structure of a high electron mobility n-type copolymer [P(NDI2OD-T2)] as studied by Infrared Transition Moment Orientational Analysis [IR-TMOA] — ●ARTHUR MARKUS ANTON¹, ROBERT STEYRLLEUTHNER², WILHELM KOSSACK¹, DIETER NEHER³, and FRIEDRICH KREMER¹ — ¹Institut für Experimentelle Physik I, Universität Leipzig, Germany — ²Fachbereich Physik, Freie Universität Berlin, Germany — ³Institut für Physik und Astronomie, Universität Potsdam, Germany

To investigate the molecular order in thin layers of P(NDI2OD-T2) a novel technique, named Infrared Transition Moment Orientational Analysis (IR-TMOA), is employed. Structure-specific vibrational bands are analyzed in dependence on *polarization and inclination* of the sample film with respect to the optical axis. Making use of IR specificity we deduce the molecular order parameter tensor for the respective moieties with regard to the sample coordinate system and determine separately the orientation of atomistic planes defined through the naphthalenediimide (NDI) and bithiophene (T2) units relative to the substrate, and hence, relative to each other. We observe that chlorobenzene causes the T2 planes to align preferentially parallel to the substrate at an angle of 29°. A chloronaphthalene:xylene mixture, instead, gives rise to a reorientation of the T2 units from a *face on* into an *edge on* arrangement (65 to 70°). In contrast, the NDI part remains basically unaffected. For both solvents, evidence for aggregated chains is observed by UV/vis absorption spectroscopy [Steyrleuthner et al., *J. Am. Chem. Soc.* **136** (2014)].

CPP 16.9 Tue 11:45 C 130

Aerosol Jet-Printed Organic Thin Film Transistors - Performance Analysis and Optimization — ●ARNO JOHN, HANNA KRIKCIOKAT, and KLAUS MEERHOLZ — Institut für Physikalische Chemie, Universität Köln

For the success of organic thin film transistors (OTFTs) in industrial applications it is essential to process devices by printing in order to radically lower production costs. Aerosol jet is a direct-write printing method which provides the user great control over material deposition. Along with layout flexibility and material compatibility, this makes this printing technology an excellent tool for fast prototyping devices.

We use aerosol jet technology to fabricate entire p- and n-type OTFTs by printing Ag-ink (source/drain electrodes), PTAA (p-type semiconductor) and N2200 (n-type semiconductor), PMMA (dielectric) and PEDOT:PSS (gate electrode). By varying parameters for individual components and evaluating the resulting transistors we optimize the printing process.

The performance of printed components is compared to evaporated and spin coated transistor components. We show that, with optimized processing parameters, it is possible to print transistors with charge carrier mobility, output current on/off ratio and threshold voltage of nearly equal quality of non-printed transistors.

CPP 16.10 Tue 12:00 C 130

Investigation of semiconducting polymers with thermally cleavable side chains for application in multilayer de-

vices I: Morphology and OFET devices. — ●JANUSZ SCHINKE^{1,2}, SABINA HILLEBRANDT^{2,3}, MILAN ALT^{2,5}, TORBEN ADERMANN^{2,4}, TOBIAS GLASER^{2,3}, ANNEMARIE PUCCI^{2,3}, NORMAN MECHAU^{2,5}, MANUEL HAMBURGER^{2,4}, WOLFGANG KOWALSKY^{1,2}, and ROBERT LOVRINCIC^{1,2} — ¹TU Braunschweig, IHF, Germany — ²InnovationLab GmbH, Heidelberg, Germany — ³U. Heidelberg, KIP, Germany — ⁴U. Heidelberg, OCI, Germany — ⁵KIT, Germany

Conjugated polymers enable the production of electronic devices from solution at room temperature due to their advantageous combination of their electrical, optical and film-forming properties. A major milestone for this emerging technology consists in achieving printed multi-layer functional devices. A great challenge for printed organic electronics is to deposit the subsequent layer of a multilayer component from the same solvent without destroying the underlying freshly deposited layer. The solubility reduction of semiconducting molecules by the external stimulus of heat is the aim of our work. Novel organic semiconductors bearing thermally cleavable side chains were investigated via AFM, ellipsometry, PE spectroscopy and IR spectroscopy. Their charge transport characteristics were studied using OFETs. These methods allow us to obtain a clear understanding of the pyrolysis process and its influence on the resulting performance. We achieve very homogeneous layers after thermal treatment which exhibit excellent solvent resistance and additionally show an increase in OFET performance.

CPP 16.11 Tue 12:15 C 130

Following the evolution of nanomorphology in PEDOT:PSS electrodes in-situ — ●CLAUDIA PALUMBINY¹, FENG LIU², THOMAS P. RUSSELL², ALEXANDER HEXEMER³, CHENG WANG³, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching — ²University of Massachusetts Amherst, Department of Polymer Science and Engineering, 120 Governors Drive, Amherst, MA 01003, USA — ³Lawrence Berkeley National Lab, Advanced Light Source, 1 Cyclotron Road, Berkeley, CA 94720, USA

The strongest advantages of organic photovoltaics over classical semiconductors are the possibility of fully flexible devices and easy up-scaling, e.g. by slot-die printing. For fully printed and flexible devices there is a strong need for non-brittle and solvent processed electrodes, such as highly conductive PEDOT:PSS. Film properties are strongly correlated to the films nanomorphology and with this strongly depend on the processing technique used. We investigate the film evolution of highly conductive PEDOT:PSS in-situ during the printing process. We monitor the film evolution by in-situ grazing incident wide angle scattering (GIWAXS). Five film formation processes are detected, the crystallization of the polymers is correlated to solvent evaporation and enhanced interchain coupling is induced by the use of high boiling point co-solvents as ethylene glycol. The enhanced conductivity in co-solvent treated PEDOT:PSS films is related to enhanced interchain coupling, change of the PEDOT to PSS ratio and crystallite sizes.

[1] Palumbiny et al., *J. Phys. Chem. C* 2014, 118, 13598.

CPP 16.12 Tue 12:30 C 130

Angle resolved spectroscopy resolving local morphology of organic optoelectronic materials — ●MARIUS VAN DEN BERG, ANKE HORNEBER, KATHRIN SWIDER, MARTIN MEIXNER, and DAI ZHANG — ¹Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany

The main component on which organic photovoltaic, transistor and photodetectors rely is the optoelectronic material. Knowledge about the local photophysical and photochemical properties of these materials at nanometer scale is important for improving overall performance and applicability [1]. The crystallinity and domain size of the local donor/acceptor morphology strongly affect the photon-electron conversion efficiencies of organic photovoltaics [2,3]. We aim at understanding the influences of nanometer scale morphology on the photophysical processes between donors and acceptors using a home built parabolic mirror assisted microscope. Using polarized excitation spectroscopy and angle resolved photoluminescence spectroscopy, we determine the relative degree of local structural order and molecular orientation in intact and photo degraded optoelectronic polymers. Furthermore, intensity changes in the angle resolved photoluminescence signals are compared with changes in the local photocurrent, to investigate morphology related photo degradation procedures, as well as the reversible/irreversible degradation steps in pi-conjugated polymers. 1)A. Dupuis et al. *Eur. Phys. J. Appl. Phys.* **56**, 34104 (2011) 2)X. Wang et al. *Small*, **7**, 2793 (2011) 3)R. Noriega et al. *Nat. Mater.*, **12**, 1038-1044, (2013)

CPP 16.13 Tue 12:45 C 130

Multifunctional SNOM and its Application in Imaging Optoelectric Materials — ANKE HORNEBER, MARIUS VAN DEN BERG, MARTIN MEIXNER, KATHRIN SWIDER, and •DAI ZHANG — Institute of Physical and Theoretical Chemistry, University of Tübingen

Optoelectronic polymer material is the basic component in photovoltaic, photodetector, or transistor system. In organic photovoltaic, the photon-electron conversion efficiency is strongly influenced by the local donor/acceptor morphology, such as crystalline, or domain size.

To get insight into this topic, we developed multifunctional scanning near-field microscopy allowing simultaneously collecting correlated topographical, optical (Raman scattering and fluorescence), and pho-

to-current signals with nanometer scale resolutions [1-3]. The distributions and local morphology of donor or acceptor materials are imaged using the Raman fingerprints and scanning probe microscopes. The intensity ratios between the donor photoluminescence and the local photocurrent will be discussed, with respect to the charge transfer processes in films of different morphologies. Furthermore, photodegradation will be compared, especially in the aspects of local morphology, and optical properties. References: [1] Zhang, D. et al, Phys. Rev. Lett., 2010, 104, 056601. [2] Wang, X., Azimi, H., Zhang, D., et al, Small, 2011, 7, 2793. [3] Wang, X., Egelhaaf, H., Zhang, D., Adv. En. Mater, 2014, 1400497. [4] Wang, X., Broch K., Zhang, D. et al., J. Phys. Chem. Lett., 2014, 5, 1048.