

**DS 5: Organic Electronics and Photovoltaics II (joint session with CPP, HL, O)**

Simulations, Polymers, Solar Cells

Time: Monday 15:00–18:00

Location: ZEU 222

DS 5.1 Mon 15:00 ZEU 222

**Quantumchemical Calculation of Zn-Porphyrine-Indolocarbazole-Conjugates** — ●KSENIA KORSHUNOVA and WICHARD J. D. BEENKEN — Technische Universität Ilmenau, Institut für Physik, Ilmenau, Germany

We have investigated the structure of Zn-porphyrin-indolocarbazole conjugates with a different number of indolocarbazole meso-substituents without and with THF and DMF axial ligands by quantumchemical methods in order to interpret experimental data such as Absorption spectra, fluorescence lifetime and quantum yields in different solutions. Contrarily to our expectations, we found very weak deformation the Zn-porphyrin macrocycle under the influence of axial THF and DMF ligands, which only tend to pull the central Zn-atom out of its equilibrium position in the macrocycle plane. This means that the very different fluorescence yields for Zn-porphyrin-indolocarbazoles in toluene, THF, and DMF cannot be explained by a conformational change.

DS 5.2 Mon 15:15 ZEU 222

**Estimating Coulomb model parameters in organic molecules from first principles** — ●IRINA PETRESKA<sup>1,2</sup>, LJUPCO PEJOV<sup>2</sup>, LJUPCO KOCAREV<sup>3,4</sup>, and GERTRUD ZWICKNAGL<sup>1</sup> — <sup>1</sup>Institut für Mathematische Physik, Technische Universität Braunschweig, 38 106 Braunschweig, Germany — <sup>2</sup>Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, 1 000 Skopje, Republic of Macedonia — <sup>3</sup>Macedonian Academy of Sciences and Arts, Skopje, Republic of Macedonia — <sup>4</sup>Faculty of Computer Science and Engineering, Ss. Cyril and Methodius University, 1 000 Skopje, Republic of Macedonia

The Coulomb parameters are estimated from electronic structure calculations based on Density Functional Theory (DFT). Of particular interest are phenylene ethynylene oligomers exhibiting electric-field controlled conductance switching. The charge transport properties are analyzed adopting a simplified two-site model accounting for Coulomb correlation effects. The Coulomb parameters are deduced from a population analysis. The DFT calculations employ a combination of the Becke's three parameter adiabatic connection exchange functional (B3) with the Lee-Yang-Parr correlation one (LYP). The Kohn-Sham SCF equations are iteratively solved using the LANL2DZ basis set, for orbital expansion, on an "ultrafine" grid for numerical integration.

DS 5.3 Mon 15:30 ZEU 222

**Theoretical Study of Simultaneous Electron- and Excitation Energy Transfer in a Fullerene-Chromophore Complex** — ●THOMAS PLEHN, JÖRG MEGOW, and VOLKHARD MAY — Humboldt-Universität zu Berlin, Germany

Mainly during the last decade fullerene based molecular systems have been of increasing interest with regard to future components in dye sensitized solar cells and artificial photosynthetic systems. This theoretical study focuses on the characteristic photoinduced charge separation process in a supramolecular complex containing a single fullerene and six pyropheophorbide-a molecules. For this purpose the excitation energy transfer processes are treated among the six chromophores. Simultaneously electron transfer takes place from the excited chromophores to the fullerene. The whole investigation uses molecular dynamics simulations of the highly flexible complex in explicit solvent environment. The transfer phenomena are described in terms of a special mixed quantum-classical version of the Förster- [1] and the well-known classical Marcus rate. Finally the charge separation process is computed concerning an ensemble of complexes. The resulting dynamics are in very good agreement with appropriate experimental data [2].

[1] J. Megow et al., ChemPhysChem 2011, 12 645-656

[2] M. Regehly et al., J. Phys. Chem. B 2007, 111, 998

**Invited Talk**

DS 5.4 Mon 15:45 ZEU 222

**Controlled crystallization of semiconducting polymer thin films** — ●SABINE LUDWIGS — Institute for Polymer Chemistry, University of Stuttgart, Germany

The talk will give an overview over current activities in my team on the morphological control of semiconducting polymers for applications in polymer electronics. Different methods to induce and control crys-

talline order over large areas in thin films will be presented. These include swelling and deswelling in defined solvent vapour atmospheres of good solvents and crystallization under confinement and with external fields. Regarding polymer materials we are currently extending our studies from conventional p-type semiconductors based on pure thiophenes like P3HT[1] to high performance p-type low bandgap polymers such as PCPDTBT[2] and n-type polymers such as PNDI2OD-2T[3]. The control of molecular orientation over macroscopic distances allows us to study the relationship between the polymer microstructure and the resulting charge transport properties along specific crystallographic directions.

[1] E. Crossland, K. Tremel, F.S.U. Fischer, K. Rahimi, G. Reiter, U. Steiner, S. Ludwigs, Adv. Mater. 2012, 24, 838. [2] F.S.U. Fischer, K. Tremel, A.-K. Saur, S. Link, N. Kayunkid, M. Brinkmann, D. Herrero-Carvajal, J. T. López Navarrete, M. C. Ruiz Delgado, S. Ludwigs, Macromolecules 2013, 46, 4924. [3] K. Tremel, F.S.U. Fischer, N. Kayunkid, R. DiPietro, R. Tkachov, A. Kiri, D. Neher, S. Ludwigs, M. Brinkmann, Charge Transport Anisotropy in Highly Oriented Thin Films of the Acceptor Polymer P(NDI2OD-T2), submitted.

**15 min break**

DS 5.5 Mon 16:30 ZEU 222

**Conjugated oligomers near surfaces with different physical and chemical nature: MD simulation of adsorption layers** — ●OLGA GUSKOVA<sup>1</sup> and JENS-UWE SOMMER<sup>1,2</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden — <sup>2</sup>Technische Universität Dresden, Institut für Theoretische Physik, Zellescher Weg 17, D-01062 Dresden

Atomistic molecular dynamics simulations are used to explore some general principles of 2D supramolecular organization of conjugated oligomers on adsorbing substrates. Two systems are studied: (i) terminally substituted dicyanovinyl quaterthiophenes, prototypic absorbers for small molecule organic solar cells on a silica surface [1] and (ii) 2,5-dialkoxy-phenylene-thienylene-based oligomers on epitaxial monolayer graphene [2]. We demonstrate that the driving force of molecular orientation on substrate is embodied by the chemical nature of the surface and the character and position of functional groups the conjugated molecule bearing, i.e. the underlying balance of forces defines the spatial orientation - standing upright or lying-down molecules on substrates. This force balance clearly allows isolated molecules to explore flat, bent or twisted molecular conformations and to exploit force anisotropies to maximize their interactions when crystals are growing. [1] O.A. Guskova et al. // J. Phys. Chem. C 2013. V. 117. P. 17285. [2] R. Shokri et al. // J. Am. Chem. Soc. 2013. V. 135. P. 5693.

DS 5.6 Mon 16:45 ZEU 222

**Frank elastic constants in nematic mesophases of polymeric semiconductors** — ●PATRICK GEMÜNDE, KURT KREMER, and KOSTAS CH. DAOULAS — Max Planck Institute for Polymer Research, Mainz

Liquid crystalline (LC) mesophases of polymeric semiconductors[1] can facilitate material processing. We develop a particle-based modeling approach considering poly(alkylthiophenes) as a test system for studying nematic mesophases. The method uses "soft tube" representations of chains where non-bonded potentials are defined by soft, directional interactions.[2,3] Here, we focus on Frank elastic constants (FC). Calculating FCs is important for comparing material properties from the soft model with experiments, studying theoretical questions related to FCs in polymer nematics and linking particle-based and continuum descriptions of LCs. We calculate FCs related to bend, splay and twist deformations from the fluctuations of the local nematic director. Indeed, the magnitudes of the FCs from our simulations agree with experiments on polymer nematics. We study the dependence on system parameters, e.g. chain length, and compare with predictions by analytical field theory.[4] Eventually we study local density fluctuations in the nematic samples, which, as predicted by theory, lead to an anisotropic scattering pattern and can be related to the elastic properties.

[1] Ho et al., Macromolecules 43, 7895 (2010) [2] Gemünden et al.,

Macromolecules 46, 5762 (2013) [3] Daoulas et al., J. Phys.: Condens. Matter 24, 284121 (2012) [4] Le Doussal & Nelson, Europhys. Lett. 15, 161 (1991)

DS 5.7 Mon 17:00 ZEU 222

**Modeling LC mesophases in polymeric semiconductors with soft directional interactions** — PATRICK GEMÜNDE<sup>1</sup>, CARL POELKING, KURT KREMER, DENIS ANDRIENKO, and ●KOSTAS DAOULAS — Max Planck Institute for Polymer Research, Mainz

Often in Soft Matter mesoscale behavior couples across a hierarchy of scales to details of molecular architecture and interactions. When modeling such materials, features accounting for the latter must be included even in drastically coarse-grained (CG) representations. Focusing on liquid crystalline (LC) mesophases of polymeric semiconductors, we highlight a top-down strategy for developing such models, projecting classical density functionals on particle-based representations. Poly(3-alkylthiophenes) (P3AT) are considered as an example. Two different CG models are developed, representing: a) the polymer chain with a "soft" flexible tube [1] and b) each alkylthiophene as a plate-like object [2]. The first describes uniaxial nematics and the second captures biaxial nematic ordering, mimicking effects of anisotropy in microscopic interactions and chain architecture. We demonstrate that the model reproduces realistic material properties in nematic mesophases. In biaxial morphologies we discuss how collective orientation and planarization of molecules affects the lengths of conjugated segments, defined via conjugation-breaking torsional defects [3]. First results on the interplay between nematic ordering and phase separation in blends of P3AT with nanoparticles are presented.[1] Daoulas et al, J. Phys.: Condens. Matter (2012) 24, 284121 [2] Gemünden et al, Macromolecules (2013) 46, 5762 [3] Rühle et al, J. Chem. Phys. (2010) 32, 134103.

DS 5.8 Mon 17:15 ZEU 222

**Correlating structural order and morphology with transport properties in donor-acceptor block copolymers for organic photovoltaics** — ●GAURAV GUPTA<sup>1</sup>, CHETAN RAJ SINGH<sup>2</sup>, RUTH LOHWASSER<sup>3</sup>, PETER MULLER BUSCHBAUM<sup>4</sup>, MUKUNDAN THELEKKAT<sup>3</sup>, HARALD HOPPE<sup>2</sup>, and THOMAS-THURN ALBRECHT<sup>1</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, Germany — <sup>2</sup>Technische Universität Ilmenau, Germany — <sup>3</sup>University of Bayreuth, Germany — <sup>4</sup>Technische Universität München, Germany

Microphase separated donor-acceptor block copolymers are promising systems for morphology control in OPV's. A nanostructure on exciton diffusion length scale, crystalline order and percolating pathways for charge transport are pre-requisites for obtaining good device properties. We here present a systematic study of the correlation between structure and charge transport in thin films of P3HT-b-PPerAcr after different thermal treatments. Combining AFM, microscopy and GISAXS we show that films annealed in the melt state above the melting temperatures of both components form typical microphase separated structures oriented parallel to the substrate, while films crystallized from the disordered state as obtained from spin coating show no well-defined microphase separated structures. GIWAXS measurements reveal that crystallization from the ordered state leads to strongly textured samples. Charge carrier mobilities as measured by SCLC were

improved by 2 orders of magnitude in films crystallized from the disordered state, the unfavorable orientation of the microphase morphology in melt annealed films resulted in poor device performance.

DS 5.9 Mon 17:30 ZEU 222

**Origins of Reduced Nongeminate Recombination in P3HT:PCBM Organic Solar Cells** — ●MICHAEL C. HEIBER<sup>1</sup>, JULIEN GORENFLOT<sup>1</sup>, VLADIMIR DYAKONOV<sup>1,2</sup>, and CARSTEN DEIBEL<sup>1</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>ZAE Bayern, 97074 Würzburg

Understanding the nongeminate recombination processes that are the dominant loss mechanisms in organic solar cells is critical to improving device performance. In P3HT:PCBM blends, nongeminate recombination has been found to be significantly slower than expected from Langevin theory and also exhibits super-second order kinetics. Several theories for this behavior have been proposed, but a complete model has not yet been reached. To shed light on this problem, we have used a combination of transient absorption spectroscopy experiments and kinetic Monte Carlo simulations. By modeling the temperature dependence of the polaron transients measured in both neat P3HT films and annealed P3HT:PCBM blend films, we demonstrate the effects of phase separation, carrier trapping, and charge transfer states on the magnitude of the recombination rate. Furthermore, we show that while neat P3HT films exhibit second order recombination and mobility behavior indicating a Gaussian density of states (DOS), P3HT:PCBM blends are complicated by super-second order recombination that is indicative of an exponential DOS and mobility measurements that are consistent with a Gaussian DOS. To unify these observations, we show that a separate distribution of charge transfer states must be included.

DS 5.10 Mon 17:45 ZEU 222

**Model systems for interchromophoric interactions in conjugated polymer materials** — ●THOMAS STANGL<sup>1</sup>, DANIELA SCHMITZ<sup>2</sup>, KLAAS REMMERSSEN<sup>2</sup>, DOMINIK WÜRSCH<sup>1</sup>, FLORIAN STEINER<sup>1</sup>, SIGURD HÖGER<sup>2</sup>, JAN VOGELSANG<sup>1</sup>, and JOHN LUPTON<sup>1</sup> — <sup>1</sup>Universität Regensburg, Regensburg, Deutschland — <sup>2</sup>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 electronic aggregation between two oligomers with different well-defined distances and single polymer chains. It is concluded that the model systems can be used to investigate the impact of H-aggregation as a function of interchromophoric distance by simultaneous measurement of lifetime and single-molecule spectra. This reveals a strong heterogeneity in coupling strengths even for identical single molecules. Further, it is shown that the coupling strength varies over time on a single molecule, leading to the conclusion that electronic aggregation has to be understood as a dynamic property. In bulk polymer films, such interchromophoric coupling impacts the functionality, e.g. the emission color 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.