

DS 15: Organic electronics and photovoltaics: simulations and optics I (jointly with CPP, HL, O)

Time: Tuesday 9:30–11:15

Location: H 2032

DS 15.1 Tue 9:30 H 2032

Excited states of terminally dicyanovinyl-substituted oligothiophenes and C₆₀: Frenkel vs. charge-transfer excitons — •BJÖRN BAUMEIER¹, DENIS ANDRIENKO¹, and MICHAEL ROHLFING² — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²Department of Physics, University of Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany

Excited states of terminally dicyanovinyl-substituted oligothiophenes (DCVnT) and C₆₀, a donor-acceptor combination used in state-of-the-art small-molecule-based organic photovoltaic devices, are studied using *ab initio* many-body Green's functions theory within the GW approximation and the Bethe-Salpeter equation. Calculations including resonant-antiresonant transition coupling and dynamical screening for DCVnT monomers yield excitation energies in excellent agreement with spectroscopic data. More importantly, it is possible with this approach to explicitly treat excited states in model dimers of DCVnT and C₆₀. This in particular allows to gain nanoscale insight into the relative energies of local (Frenkel) and charge-transfer excitations, which influence the charge generation in devices.

We will present results for model systems of DCV4T:C₆₀ and DCV5T:C₆₀ and will analyze the dependence of the relative excitations on, e.g., the arrangement of donor and acceptor molecules in the dimer and the length of the donor, as well as discuss the consequences for performance in organic photovoltaic devices.

DS 15.2 Tue 9:45 H 2032

Microscopic simulations of charge transport in disordered organic semiconductors — •DENIS ANDRIENKO, BJOERN BAUMEIER, FALK MAY, MANUEL SCHRADER, and VICTOR RUEHLE — Max Planck Institute for Polymer Research, Mainz, Germany

Charge carrier dynamics in an organic semiconductor can often be described in terms of charge hopping between localized states. The hopping rates depend on electronic coupling elements, reorganization energies, and driving forces, which vary as a function of position and orientation of the molecules. The exact evaluation of these contributions in a molecular assembly is computationally prohibitive. Various, often semi-empirical, approximations are employed instead. In this work, we review some of these approaches and introduce a software toolkit which implements them.¹ The purpose of the toolkit is to simplify the workflow for charge transport simulations, provide a uniform error-control for the methods, flexible platform for their development, and eventually allow in silico pre-screening of organic semiconductors for specific applications. All implemented methods are illustrated by studying charge transport in amorphous films of tris(8-hydroxyquin)aluminium, a common organic semiconductor.

¹ V. Rühle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier, D. Andrienko, J. Chem. Theory Comput., 7, 3335 (2011)

DS 15.3 Tue 10:00 H 2032

Migration of singlet excitons in thin films of oligothiophene molecules — •JENS LUDWIG, SUSANNE HINTSCHICH, HANNAH ZIEHLKE, KARL LEO, and MORITZ RIEDE — Institut für Angewandte Photophysik, Technische Universität Dresden, 01069 Dresden, Germany

In organic materials, such as thin amorphous films of oligothiophenes, localized singlet excitons constitute the primary photoexcitations. Via Förster Resonant Energy Transfer (FRET) they migrate between different molecular sites, represented by an inhomogeneously broadened density of states (DOS).

Dispersive exciton migration in thin films of dicyano-substituted terthiophenes is probed by time resolved spectroscopy using a streak camera and simulated with a Monte-Carlo program based on thermally activated hopping of excitons. The time-resolved spectral relaxation and its temperature dependence, as well as the energy dependent decay curves are consistently described within this picture. Side chains appended to the backbone of the oligothiophenes impact the morphology and average intermolecular distance and hence significantly influence the efficiency of exciton migration. In this presentation, oligothiophene derivatives with different side chains are compared regarding their exciton dynamics in thin films. We also consider energy transfer to C₆₀ in

blend layers with the terthiophene derivatives, leading to a very fast quenching of luminescence from the terthiophene molecules.

DS 15.4 Tue 10:15 H 2032

Vibrational Davydov-splittings in oriented organic semiconductor crystals: polarization-dependent measurements versus theoretical calculations — •TOBIAS BREUER¹, MALI CELIK², PETER JAKOB³, RALF TONNER², and GREGOR WITTE¹ — ¹AG Molekulare Festkörperphysik — ²AG Theoretische Oberflächenchemie — ³AG Oberflächenphysik, Philipps-Universität Marburg, D-35032 Marburg

Vibrational properties of highly ordered crystalline perfluoropentacene (PFP) films epitaxially grown on KCl(100) and NaF(100) substrates have been studied by means of transmission infrared spectroscopy and density functional theory. The different molecular orientations adopted by PFP on both substrates (standing vs. lying) and their epitaxial ordering [1] enable precise polarization-resolved measurements along individual crystallographic directions and thus allow an unambiguous experimental determination of the polarizations of the IR modes. Computations of the vibrational spectra beyond the single-molecule approximation were employed at the periodic dispersion-corrected density functional level (PBE-D2PBC) and compared to non-periodic calculations (PBE/def2-TZVPP). Thereby, a comparison between experiment and different theoretical models was enabled. A microscopic explanation for the experimentally observed Davydov splitting of some modes and the IR-inactivity of others was derived, based on the mutual coupling of the dynamical dipole moments of the two molecules within the unit cell.

[1] T. Breuer et al., Phys. Rev. B 83, 155428 (2011).

DS 15.5 Tue 10:30 H 2032

XPS investigation of charge transfer complexes with strong donor / acceptor molecules: composites and interfaces — •SEBASTIAN STOLZ, ERIC MANKEL, JULIA MAIBACH, THOMAS MAYER, and WOLFRAM JAEGERMANN — Technische Universität Darmstadt, Materials Science Institute, Surface Science Division, Petersenstraße 32, 64287 Darmstadt, Germany

Organic charge transfer complexes like TTF-TCNQ have raised interest due to their electronic and optical properties being highly sensitive to small variations of the molecular constituents. In this manner, the electrical properties of TTF-TCNQ and its derivatives vary significantly, and hence different applications for organic electronic devices are imaginable. Thin film layers of DBTTF-TCNQ were prepared in UHV and inert atmospheres respectively to avoid contamination. Preparation methods used were (1) evaporation of solution grown crystals, (2) drop casting under Ar atmosphere, and (3) co-evaporation of the individual molecules with varying donor / acceptor ratios. Additionally, DBTTF was deposited stepwise onto a clean TCNQ substrate in order to investigate the reaction mechanism. The resulting thin films were analyzed by in-situ photoemission spectroscopy, partially carried out at the U49/2 beamline at Bessy II. The stoichiometric ratio of donor and acceptor molecules was determined and the formation of the CT-complex was confirmed for all samples. In case of a stoichiometric ratio unequal to 1:1, the spectra show a mixture of the CT-complex and neutral excess molecules. Finally, the experimentally determined spectra were compared to DFT-calculations.

DS 15.6 Tue 10:45 H 2032

A new differential reflectance spectroscopy method with enhanced sensitivity — •HARALD ZAGLMAYR, LIDONG SUN, and PETER ZEPPENFELD — Institute of Experimental Physics, Johannes Kepler Universität, Linz, Austria

Differential reflectance spectroscopy (DRS), measures the normalized difference of the reflectance of the bare and adsorbate covered surface, respectively. The technique possesses enhanced surface sensitivity and is thus widely used for the in-situ study of organic thin film growth [1,2]. The signal to noise ratio of the obtained spectra, which determines the sensitivity of the method, strongly depends on the stability of the light source. Here, we introduce a new method to overcome the influence of the instability of the light source by normalizing the spectrum of the reflected beam with that of the incident beam, which

are measured simultaneously. Our approach shows a drastic improvement of the signal to noise ratio of the DR spectra. The new instrument has been successfully applied to monitor the in-situ growth of alpha-sexithiophene (α -6T) and cobalt-tetramethoxyphenylporphyrin (Co-TMPP) on the Cu(110)-(2x1)O reconstructed surface. The details of the technical realization and the scientific results concerning the organic thin film growth will be reported in this contribution.

[1] R.Forker, T.Fritz; Phys. Chem. Chem. Phys., 2009, 11, 2142-2155

[2] U.Heinemeyer *et al.*; Phys. Rev. Lett., 2001, 104, 257401

DS 15.7 Tue 11:00 H 2032

Interface Effects on the Glass Transition in Thin Polystyrene Films studied with High Temperature Single Molecule Fluorescence Microscopy —

•DOMINIK WÖLL¹, BENTE FLIER², MORITZ BAIER², KLAUS MÜLLEN³, STEFAN MECKING², and ANDREAS ZUMBUSCH² — ¹Zukunftscolleg, Universität Konstanz, Germany — ²Fachbereich Chemie, Universität Konstanz, Germany —

³Max-Planck-Institut für Polymerforschung Mainz, Germany

The glass transition is a ubiquitous phenomenon in many materials. Despite its high importance and considerable research efforts, a full understanding of this property is still lacking. In thin polymer films, interfaces complicate things as they alter the glass transition in their vicinity. Experimental approaches to study the influence of interfaces on dynamics in polymers are thus very challenging. In our contribution, we present single molecule fluorescence spectroscopy as a new method to investigate such interfacial effects on the glass transition of polymers. We measured the translational diffusion coefficients of single perylene diimide molecules in thin polystyrene films up to temperatures of 150 °C and analyzed their distributions. These distributions and the number of mobile molecules depend strongly on film thickness. They can be modeled with Monte Carlo random walk simulations assuming a reduced glass transition temperature and an increased residence probability of dye molecules at the polymer surface.