

SYCT 1: Symposium Charge Transfer Effects in Molecular Materials

Time: Monday 9:30–12:00

Location: H1

Invited Talk

SYCT 1.1 Mon 9:30 H1

A coarse grained QM/MM approach for the description of charge transfer in complex systems — ●MARCUS ELSTNER — Karlsruhe Institute of Technology, Karlsruhe, Germany

Charge transfer in DNA has received much attention in the last years due to its role in oxidative damage and repair in DNA, but also due to possible applications of DNA in nano-electronics. Despite intense experimental and theoretical efforts, the mechanism underlying long range hole transport is still unresolved. We present a new computational strategy to evaluate the charge-transfer (CT) parameters for hole transfer in DNA. Based on a fragment orbital approach, site energies and coupling integrals for a coarse grained tight binding description of the electronic structure of DNA can be rapidly calculated using the approximate Density Functional method SCC-DFTB. Environmental effects are captured using a combined quantum mechanics/molecular mechanics (QM/MM) coupling scheme and dynamical effects are included by evaluating these CT parameters along extensive classical molecular dynamics (MD) simulations. The fluctuations of the counterions, strongly counterbalanced by the surrounding water, leads to large fluctuations of the site energies, which govern the hole propagation along the DNA strand, while the electronic couplings depend strongly on DNA conformation and are not affected by the solvent (2). Using this methodology, the time course of the hole can be followed by propagating the hole wave function using the time dependent Schrödinger equation for the coarse grained Hamiltonian (5,6).

Invited Talk

SYCT 1.2 Mon 10:00 H1

Identifying and resolving charge separation in organic solar cells — ●EBERHARD RIEDLE — BioMolekulare Optik, LMU München

The charge separation and the charge mobility are essential factors for efficient solar devices. Time resolved spectroscopy can resolve these processes completely. We use sub-50 fs resolution, fully tunable pump pulses, and continuum probing from 300 to 1700 nm. Since solar cells are intended to absorb visible light, particularly probing in the NIR allows to differentiate between the excitonic and polaron states. We show that the primary excitation in P3HT-Si hybrid cells are excitons located on the polymer. They dissociate to polarons in 140 fs. A significant part of the excitation is lost at this early stage due to internal conversion back to the ground state [1]. Using the knowledge from the transient measurements, we optimize the composition and preparation of the cells to an efficiency of 1.1 % [2]. The character and mobility of the polarons is determined by excitation fluence dependent measurements. In a series of polymers - mixed with C₆₀ - with increasing conjugation length, the highly structured transient spectra do not allow the easy identification of polarons. The analysis shows that the spectrum is closely related to the electroabsorption spectrum of the polymer, i.e. the derivative of the absorption spectrum. In this way we can conclude that indeed charge separation and an electric field is generated in the thin film solar cells by the visible excitation.

[1] D. Herrmann et al., *J. Am. Chem. Soc.* **133**, 18220 (2011).

[2] S. Niesar et al., *Green* **1**, 339 (2011).

Invited Talk

SYCT 1.3 Mon 10:30 H1

Quantifying the energy of charge transfer states: From molecular crystals to donor-acceptor blends — ●REINHARD SCHOLZ — Institut für Angewandte Photophysik, Technische Universität Dresden, George-Bähr Str. 1, 01069 Dresden, Germany

In molecular crystals, exciton models accounting for neutral molecular excitations and charge transfer (CT) allow to deduce their energy alignment from measured spectra.¹ Donor-acceptor blends may reveal weak CT absorption and photoluminescence spectra below the main absorption bands, and for polymer-fullerene solar cells, the respective energies correlate with the open circuit voltage.² Calculations of CT energies in these materials require computational methods with the correct asymptotics of the mutual Coulomb interaction between

pairs of ionized donor and acceptor molecules like constrained DFT schemes.³ Moreover, the solvation energy arising from the embedding polarizable medium and the screening of the Coulomb interaction result in substantial deviations from the interaction between oppositely charged donor and acceptor molecules in vacuum. Based on a constrained DFT scheme and an embedding scheme accounting for the polarizable medium, calculated CT energies for selected donor-acceptor pairs are compared to available spectroscopic data and the open circuit voltage of photovoltaic devices.

[1] L. Gisslén and R. Scholz, *Phys. Rev. B* **80**, 115309 (2009).

[2] K. Vandewal *et al.*, *Adv. Funct. Mater.* **18** 2064 (2008).

[3] M. Rapacioli, F. Spiegelman, A. Scemama, and A. Mirtschink, *J. Chem. Theory Comput.* **7**, 44 (2011).

Invited Talk

SYCT 1.4 Mon 11:00 H1

Efficient Exciton Generation and Collection in Organic Solar Cells — ●MARK THOMPSON¹, CONG TRINH¹, STEVE FORREST², and JERAMY ZIMMERMAN² — ¹University of Southern California, Los Angeles, CA, USA — ²University of Michigan, Ann Arbor, MI, USA

The exciton is a critical part of each of the processes leading to photocurrents in Organic PhotoVoltaics (OPVs), and being able to control the location, lifetime and energy of the exciton is essential to achieving high efficiency. We have investigated methods for tuning exciton energies and controlling their migration paths within a thin film. I will discuss our most recent work with both organic dyes, such as squaraines and dipyrrens as well as metallo-porphyrin materials for OPVs. This involves a careful materials design study that leads to both low energy absorption (into the nearIR) and the efficient use of multiple absorbers to efficiently harvest photons through the entire visible spectrum.

A key limiter of OPV performance is the open circuit voltage, Voc. A number of parameters control the Voc, including the energetics of the donor and acceptor, the energy of the charge transfer exciton formed at the D/A interface and the structure of the materials at the D/A interface. We have investigated methods to tailor the interfacial structure at the D/A interface, leading to improved Voc. We have investigated thermal and solvent annealing, as well as a process we call chemical annealing, where the thin film is exposed to an external agent, which is incorporated into the film stoichiometrically. I will discuss each of these methods and how they affect the device performance.

Invited Talk

SYCT 1.5 Mon 11:30 H1

Electron transport in organic single-crystal transistors and Schottky-gated heterostructures — ●ALBERTO MORPURGO — University of Geneva, Geneva, Switzerland

Organic single-crystal transistors have unprecedented quality and enable the investigation of several interesting phenomena (band-like transport in, the Hall effect, interfacial polarons, etc.). So far, virtually only p-type devices have been studied. Here, I will discuss electron transport in single-crystal FETs and heterostructures, showing how the best n-type devices perform at the level of their p-type counterparts. I will first focus on PDIF-CN2 single-crystal FETs, in which we observe the characteristic signatures of band-like transport (electron mobility increasing upon cooling and of Hall effect). The experimental results, and a comparison with p-type materials in which band-like transport in FETs is observed, suggest that the coupling of the charge carriers to the polarizability of the organic semiconductor plays a key role in determining which organic materials are more likely to exhibit band-like transport. Next, I will discuss new Schottky-gated heterostructures based on rubrene and PDIF-CN2 crystals, in which a conducting 2D layer forms spontaneously due to charge transfer. Gate-dependent transport and Hall measurements show that electrons are responsible for the conductivity, and that their density decreases linearly with decreasing temperature. We understand this behavior in terms of the heterostructure band-diagram, which quantitatively captures the slope of the linear temperature dependence. In the best devices, the electron mobility remains as high as ~ 1 cm²/Vs at T=30 K.