

Charge-Transfer Excitons at the Interface of Organic Semiconductors

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The concept of an organic photovoltaic cell relies crucially on efficient charge separation at the interface of two different organic materials [1]. Ideally, strongly bound and localized excitons which were produced by light absorption would break up to form free carriers at the interface. Due to poor dielectric screening of charge in organic materials, however, the Coulomb attraction is long-ranged and relatively strong. As a consequence, the electron and hole – even though located on opposite sides of the interface – may be trapped in a localized charge-transfer (CT) exciton state.

This presentation will discuss the observation of a Rydberg-like series of CT exciton states at the surfaces of pentacene and tetracene thin films using femtosecond time-resolved two-photon photoelectron spectroscopy (TR-2PPE). The surface of an organic thin film serves as a model system for a donor-acceptor interface where the role of the electron acceptor is taken by vacuum. The energetics of the CT excitons can be understood qualitatively in a conceptually simple Coulomb picture where the electron (in vacuum) is attracted by the image potential at the surface and the Coulomb potential of the hole [2]. Depending on the pump photon wavelength, different states from the lowest state with a binding energy around 0.4 eV up to the image potential state, representing the two-dimensional continuum, are excited. The lifetimes of the CT exciton states is of the order of 50-100 fs. Higher lying states decay rapidly into lower states [3].

[1] X.-Y. Zhu, Q. Yang, M. Muntwiler, *Acc. Chem. Res.* **42**, 1779 (2009)

[2] M. Muntwiler, Q. Yang, W. A. Tisdale, X.-Y. Zhu, *Phys. Rev. Lett.* **101**, 196403 (2008)

[3] Q. Yang, M. Muntwiler, X.-Y. Zhu, *Phys. Rev. B* **80**, 115214 (2009)