

Interfaces of organic solar cell materials

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1 The donor/acceptor interface

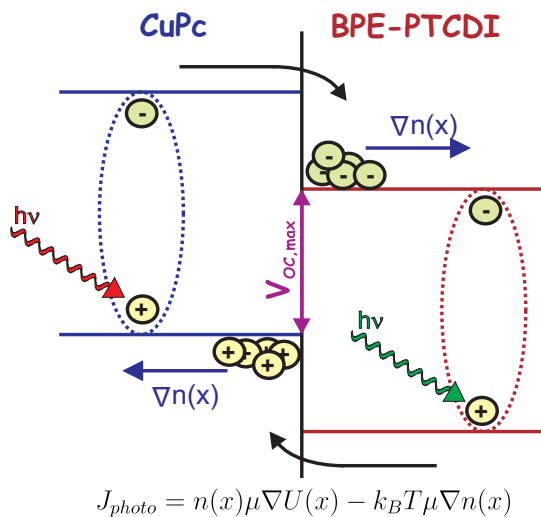


Figure 1: Working principle of a bilayer-heterojunction solar cell. $n(x)$ represents the density of photogenerated charge carriers.

Organic solar cells (OSC) promise a possible way to obtain cheap and flexible devices. Unfortunately, until now the efficiencies of OSCs are low. The prototype of a bilayer-heterojunction OSCs, the so called Tang-Cell, shows an open circuit voltage of 0.44 V and a short circuit current of 2.4 mA/cm^2 leading to an efficiency of 0.8 % only. By usage of interdigitating phases forming bulk heterojunctions and tandem cell device structures efficiencies of nearly 5 % have been reached in the laboratory.

In OSCs exciton dissociation takes place at a phase boundary between a donor type material (CuPc) and an acceptor type material (BPE-PTCDI). The conversion efficiency ($\eta \sim V_{OC} \cdot I_{SC}$) is affected by two interface parameters namely the electronic alignment between the donor HOMO and the acceptor LUMO (influences V_{OC}) and the development of the electric field at the interface (influences

I_{SC} by ∇U) as shown in Fig. 1. The ideal method for investigation of these interface properties is synchrotron induced photoelectron spectroscopy (SXPS). Our experimental station SoLiAS at BESSY II can be connected to the beamlines U49/2-PGM2 and TGM7 providing synchrotron light in the range of 90eV to 1400eV and 20eV to 120eV, respectively.

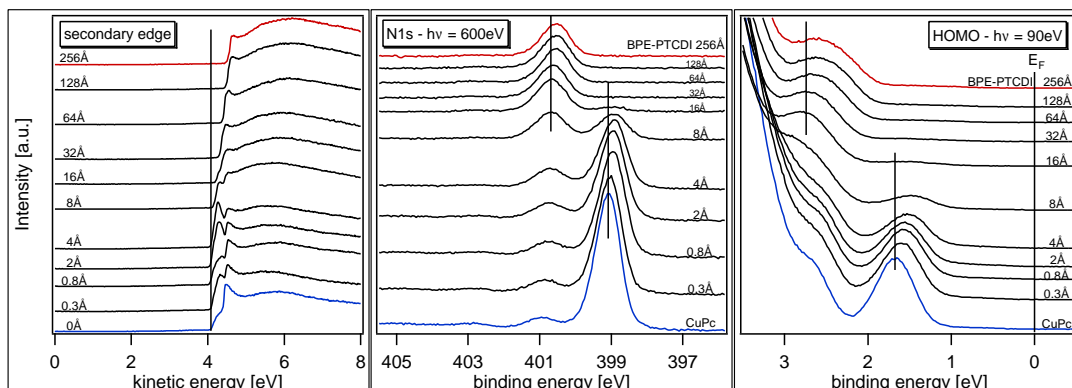


Figure 2: XPS spectra of the secondary electron edge, the N1s core level and the HOMO region taken during the stepwise deposition of BPE-PTCDI on CuPc.

The SXP spectra for step-by-step deposition of BPE-PTCDI molecules on a in-situ prepared CuPc layer is shown in Fig. 2. After each evaporation step photoemission spectra of the N1s core level line and the HOMO region in the valence band are taken at light energies of 600 eV

and 90 eV, respectively. At the beginning and at the end of the experiment the typical N1s and HOMO features of the pristine organic materials can be identified. Because of the high surface sensitivity, the intensities of the CuPc features are attenuated with increasing BPE-PTCDI coverage while the features of BPE-PTCDI are simultaneously growing. The evolution of the intensity of the CuPc emissions allows the determination of the deposition rate of BPE-PTCDI which is around $8 \text{ \AA}/\text{min}$ and of the ascribed layer thicknesses.

The N1s core level line as well as the HOMO and the secondary edge show an energetic shift of the line position relative to the Fermi energy with increasing BPE-PTCDI coverage. This shift can be correlated to a change of the electric potential at the interface. The experimental results can be translated into a band diagram of the CuPc/BPE-PTCDI interface (Fig. 3).

The band diagram shows a band bending in both phases forming barriers of 0.12 eV for electrons in BPE-PTCDI and of 0.15 eV for holes in CuPc hindering the transport after the charge carrier dissociation. The width of the space charge layer in BPE-PTCDI is around 10nm as derived from the coverage. By these electric fields the recombination of dissociated charge carriers at the interface is favoured which could be the reason for the low short circuit current of the Tang-Cell.

A suggestion for improving of the short circuit current could be doping of the CuPc layer. As shown in Fig. 3, the Fermi energy of CuPc is found at a mid gap position. A shift of the Fermi energy closer to the HOMO level could reduce the barrier height or reverse the band bending causing a potential gradient for the dissociated charge carriers accelerating them towards the contacts.

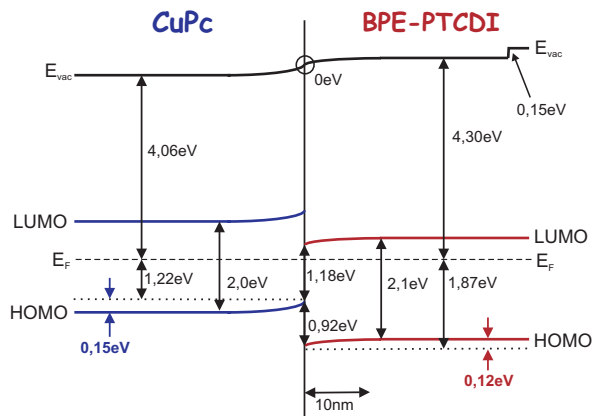


Figure 3: Band diagram of the CuPc/BPE-PTCDI interface.

2 A doping mechanism for organic layers

Typically, shifting of the Fermi energy of molecular organic layers is performed by mixing with strong acceptor molecules. Grabbing this idea we decided to coevaporate CuPc with TCNQ obtaining blends of both materials with different TCNQ content. After coevaporation we took photoemission spectra of the composites to identify the position of the CuPc HOMO and the N1s core level with respect to the Fermi energy (Fig. 4).

With increasing TCNQ content the maximum of the HOMO and the CuPc fraction of the N1s level shift towards lower binding energies. Simultaneously, the TCNQ derived part of the N1s level shifts to higher binding energies with decreasing TCNQ content. The shift of the Fermi energy closer to the CuPc HOMO level indicates p-doping of the CuPc matrix. In the following we will describe these shifts by a charge transfer model between the two organic phases.

According to the gaussian disorder model of organic semiconductors, a density of states (DOS) in the gap between the HOMO and the LUMO level is introduced in which every molecule provides one state to the continuous distribution. Due to a HOMO binding energy E_H of 1.3 eV and a gap energy of 3.1 eV in pristine CuPc, the contribution of LUMO states to the DOS of CuPc around the Fermi energy can be neglected. This leads to equation 1 in which V_{mol} is the volume per CuPc molecule and σ the standard deviation. The TCNQ LUMO can be described similarly when the HOMO maximum energy E_H is replaced by the LUMO energy E_L .

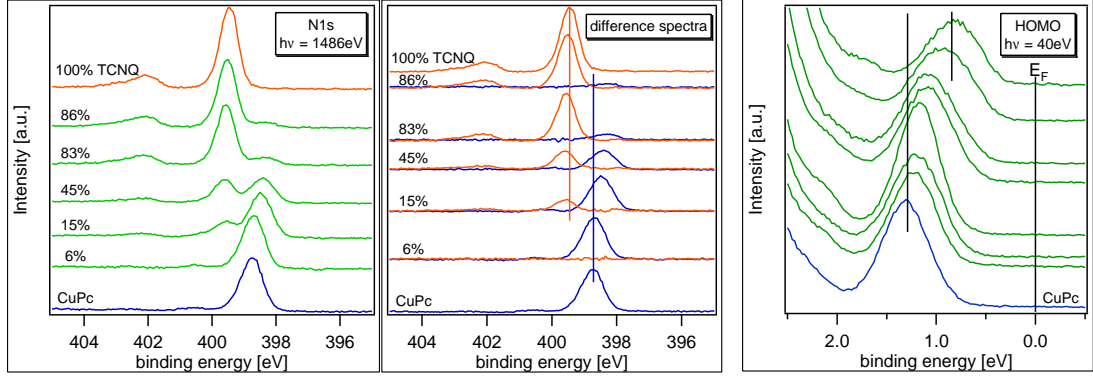


Figure 4: XP spectra of the N1s core level line and the CuPc HOMO of CuPc/TCNQ composites with varied TCNQ content. The difference spectra separate the superposing N1s emissions of CuPc and TCNQ.

$$DOS(E) = N \cdot e^{-\frac{(E-E_H)^2}{2\sigma^2}} \quad \int_{-\infty}^{\infty} DOS(E)dE = \frac{1}{V_{mol}} \quad (1)$$

Moving of the Fermi energy around its origin stands for filling and depletion of electronic states in the tails of the DOS. Due to charge neutrality the electrons taken from the CuPc DOS must be transferred to the TCNQ derived DOS. The equality of transferred charge in both phases is represented by equation 2 in which every DOS is weighted by the TCNQ content γ .

$$(1 - \gamma) \int_{E_F^0}^{\Delta E_F^{CuPc}} DOS^{CuPc} dE = \gamma \int_{\Delta E_F^{TCNQ}}^{E_F^0} DOS^{TCNQ} dE \quad (2)$$

Equation 2 determines the interdependence of the Fermi level shifts in the CuPc phase (ΔE_F^{CuPc}) and the TCNQ phase (ΔE_F^{TCNQ}) for a certain TCNQ content γ . In Fig. 5 the measured Fermi energy shifts derived from the N1s emission (dots) are compared with the best fit (lines) we obtain for a standard deviation of $\sigma = 0.25$ eV for the DOS in both phases.

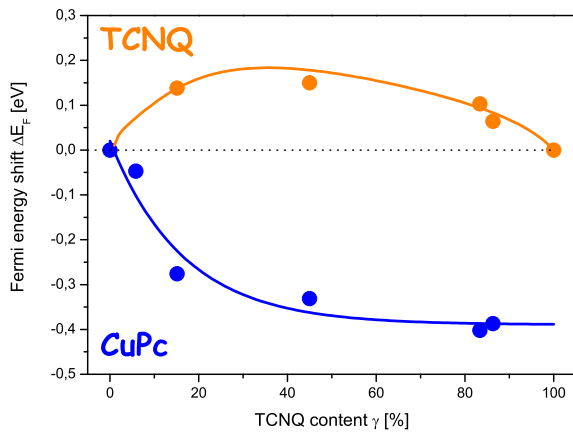


Figure 5: Fermi energy shifts of CuPc and TCNQ.

Summarizing the presented model seems to be a suitable possibility to describe the mechanism of Fermi energy shifts in doped layers of organic semiconductors. The assumptions will be validated in further experiments.

The standard deviation σ leads to a full width half maximum (FWHM) of around 550 meV for the HOMO of CuPc which is in good agreement with the measured HOMO FWHM shown in Fig. 4. For comparison the resolution of the system (SoLiAS @ TGM7, $h\nu = 40$ eV) is about 170 meV at the Fermi edge.

Due to the double occupation of each state the transferred charge carrier density can be calculated using the left hand side of equation 2 multiplied by a factor of two. The amount of transferred charge is found to be in the range of $1 \cdot 10^{17} - 1.5 \cdot 10^{18} \text{ cm}^{-3}$ leading to a fraction of around 0.05 - 0.1 % of charged molecules in each phase for a mean TCNQ content.