Molecular electrical doping is governed by intermolecular hybridization

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Current models for the fundamental process of organic semiconductor (OSC) doping with strong molecular electron-acceptors (p-dopants) are found to be inconsistent with well-established concepts in that field, such as the formation of polarons [1]. Combining Ultraviolet Photoelectron Spectroscopy (UPS), specular (XRD) and grazing-incidence x-ray diffraction (GIXRD) with theoretical calculations we address these inconsistencies for the prototypical material pair pentacene (PEN) p-doped with the widely used strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [1].

Figure 1: (a) XRD on a pure PEN film (black), a PEN film co-deposited 10:1 with F4-TCNQ (blue) and on a 1:1 blend; nominal film thickness: 30 nm. (c) GIXRD in-plane scans on the samples of (a) ($\alpha_i = \alpha_f = 0.15^\circ$); $q_z$ and $q_{||}$ denote the scattering vector components perpendicular and parallel to the substrate, respectively; data recorded at the HASYLAB beamline W1. (c) Left: UPS results in the range of $E_F$ for 20 nm PEN on SiO$_x$ (black curve), 10:1 mixed (blue curve), and 1:1 mixed (red curve) PEN:F4-TCNQ; binding energy given with respect to the vacuum level ($E_{vac}$). Right: Schematic energy-level diagram (aligned to $E_F$) and corresponding ionization energies deduced from the UPS data; data recorded at the optics beamline (SurICat) at the Helmholtz Zentrum Berlin für Materialien und Energie - BESSY II. For details see Ref. [1]

Figure 1 shows the impact F4-TCNQ admixture via vacuum co-deposition on the structure of PEN thin-films by XRD (a) and GIXRD (b) showing a significant deterioration of the film structure already for a mixing ratio of 10:1 (blue curve) and amorphous growth for the 1:1 blend. The corresponding UPS data (Figure 1c) evidences an accompanying increase of the ionization energy (IE) from 4.90 eV (pure PEN), over 5.20 eV (10:1 blend) to finally 5.75 eV (1:1). Fully in-line with our XRD results, the IE of the pure film is assigned to standing PEN and the IE value of the 10:1 blend is attributed to amorphous PEN [2]. The IE of the 1:1 mixed film, however, increased even to 5.75 eV, which is larger than the highest reported solid-state IE (for flat-lying PEN) of 5.45 eV [2]. Furthermore, UPS did not reveal any spectroscopic evidence for polaronic states, which, however, would be expected at (or close to) the Fermi Energy ($E_F$) according to the standard doping model prevalent in literature, which assigns integer charge transfer between OSC and dopant (Figure 2a) resulting in singly-occupied states (positive polarons, $P^+$) that are thought to exhibit reduced IE (Figure 2b). Most importantly, even at 1:1 ratio such states are absent in UPS, which is in-line with all published UPS data on doping of related systems, where generally lower dopant concentrations were used.
Figure 2: (a) For p-type doping, the OSC, e.g., PEN, is generally thought to be ionized via integer electron transfer (red arrow) to the dopant, e.g., F4-TCNQ. (b) Commonly observed energy-level shift upon increasing p-dopant concentration. Positive polaron states (P+) are thought to be formed in the fundamental gap of the OSC. In contrast to the valence band edge of inorganic semiconductors, $H$ has never been observed to cross $E_F$ in molecularly doped OSCs but always remains below, suggesting pinning at $P^+$. (c) Schematic energy level diagram of the proposed model for molecular electrical doping: The HOMO of PEN hybridizes with the LUMO of F4-TCNQ leading to a splitting of the energy levels into a filled bonding and an empty anti-bonding supramolecular hybrid orbital, as illustrated by the orbital isosurface plots calculated for a PEN/F4-TCNQ complex; all energy level positions drawn to scale.

To fully explain our results and the fundamental mechanism of molecular electrical p-doping in general, we suggest intermolecular orbital hybridization between the OSC HOMO and the dopant LUMO, leading to the formation of a doubly occupied bonding and an empty anti-bonding supramolecular hybrid orbital (Figure 2c), which is substantiated by density-functional theory calculations [1]. In contrast to the integer charge-transfer model prevalent in literature, upon doping with F4-TCNQ both electrons from the PEN HOMO occupy the new (bonding) hybrid orbital, rather than one electron being transferred from the PEN HOMO to the F4-TCNQ LUMO. Our calculations fully support that the hybridized PEN/F4-TCNQ complexes have a higher IE than pristine PEN, which is fully consistent with our UPS results (Figure 1c), but also indicate that they exhibit a reduced energy gap, which was experimentally validated by UV-VIS spectroscopy [1].

The present study reveals the limitations of current molecular dopants: Through the substantial offset between OSC frontier orbital and intra-gap hybrid state (Figure 2c), only a fraction of the OSC/dopant complexes is ionized at finite temperature, thus limiting the achievable maximum density of mobile charge carriers. To reach higher carrier densities without adversely affecting their mobility through a deterioration of the packing (Figure 1a, b), i.e., at lower doping concentrations, this offset must be minimized by suppressing the splitting, which is, in turn, due to electronic coupling between OSC and dopant frontier molecular orbitals. Shielding the functional core of strong molecular acceptors emerges as design strategy for improved molecular dopants in future high-performance organic electronic devices.

References
