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- fill in a separate form for each project or series of measurements.
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- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Correlating Doping Efficiency, Dopant Strength, and Intermolecular Distance in Molecular Electrical Doping of Organic Semiconductors	**Experiment number**: MA 2079
Beamline: ID10	**Date of experiment**: from: 12.12.2013 to: 18.12.2013	**Date of report**: 25.02.2014
Shifts: 18	**Local contact(s)**: Giovanni Li DESTRI, Oleg KONOVALOV	*Received at ESRF:*

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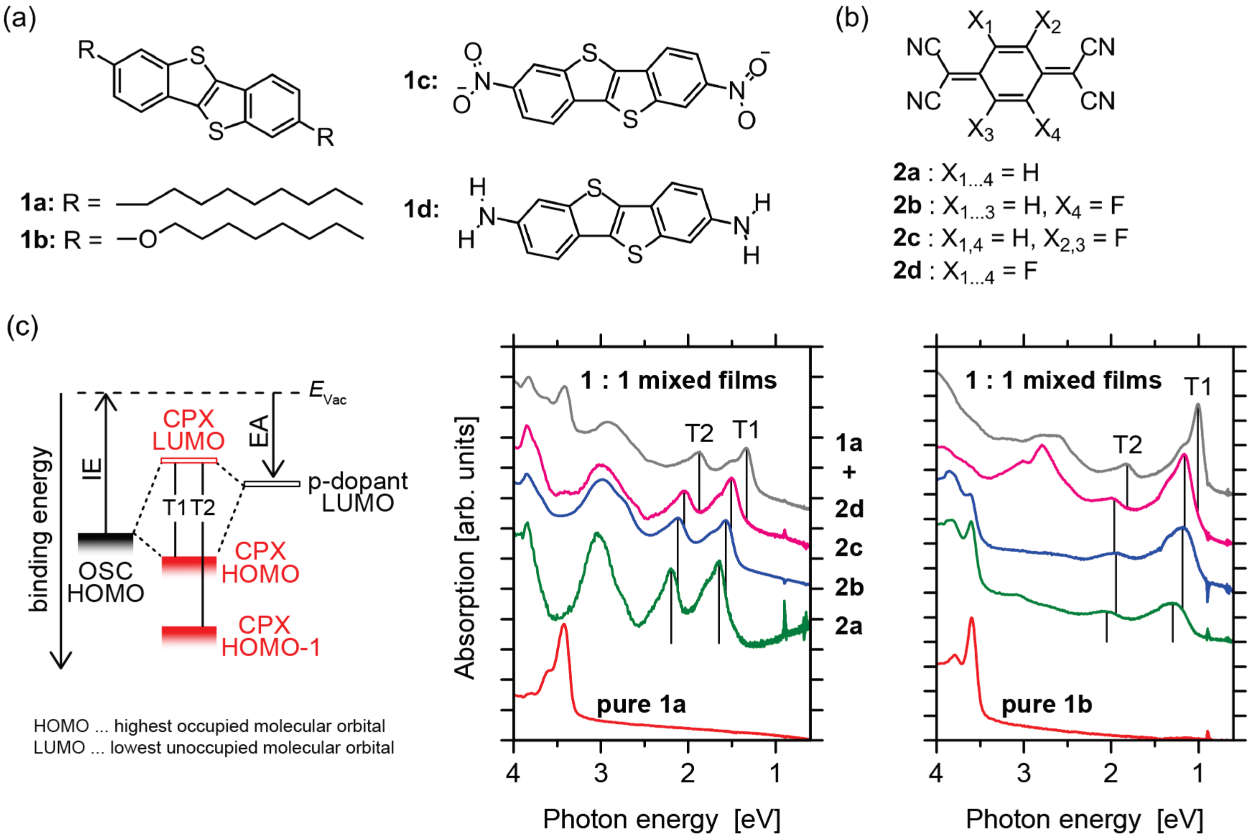
Report:

The aim of the present experiments was to refine a recently established new model on molecular electrical doping of organic semiconductors (OSCs). Instead of direct integer-charge transfer between OSC and molecular p-dopant, as commonly assumed in analogy to inorganic semiconductor doping, this model is based on frontier molecular orbital hybridization of OSC and dopant molecules forming ground-state charge transfer complexes (CPXs) [1-3]. To this end, we thoroughly pre-characterized pairs of prototypical OSCs (Fig. 1a) and p-dopants (Fig. 1b) by optical spectroscopy (Fig. 1c) in order to assess complex formation, which is deduced from the occurrence of transitions between the doubly occupied bonding (CPX-HOMO) and the empty anti-bonding (CPX-LUMO) supramolecular hybrid orbital of the CPX (transitions T1, T2 in the schematic energy level diagram in Fig. 1c).

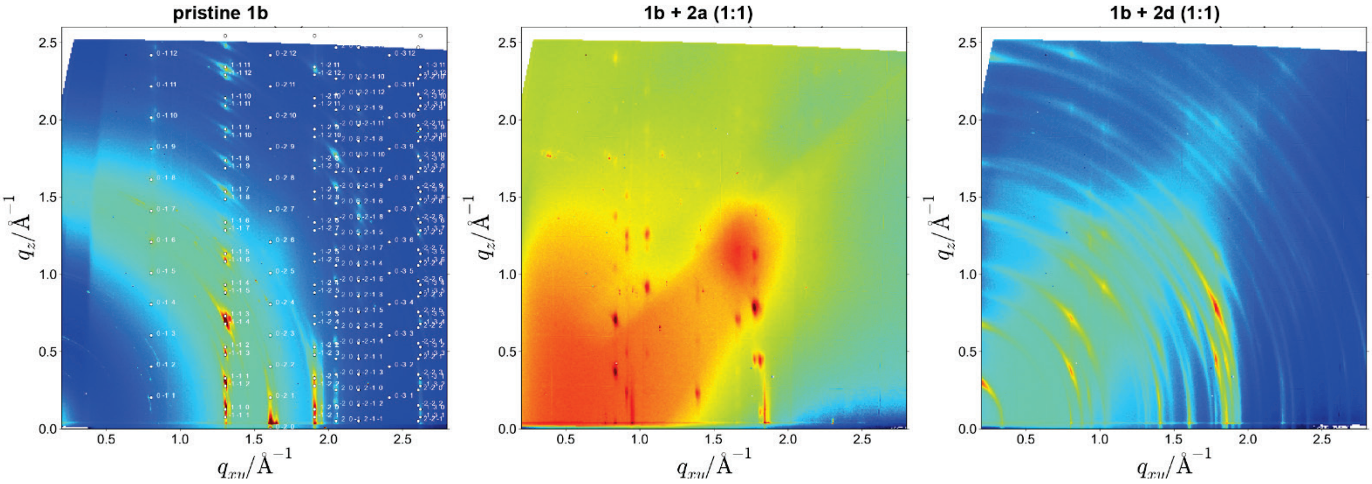
Through chemically modifying the alkylated OSC benzothieno-benzothiophene (compound **1a**) via oxygen substitution (compound **1b**), the ionization energy (IE) of the OSC could be reduced from 5.27 eV to 5.06 eV, as measured by photoelectron yield spectroscopy. Hence, while retaining an essentially identical molecular structure, the IE of the OSC is tuned into the range of the electron affinity (EA) of the p-dopant tetrafluoro-tetracyanoquinodimethane (compound **2d**), therefore, already fulfilling the desired scenario of IE $\approx$ EA (as initially aimed for with dihexyl-terthiophene in the project proposal) for the more application relevant benzothieno-benzothiophene derivative (**1b**) itself.

Figure 1



Importantly, the energy level splitting in the CPX (transitions T1, T2) turned out to be tunable by employing the differently strong dopants **2a** (EA = 4.23 eV) … **2d** (EA = 5.08 eV), as apparent from Fig. 1c, while, even in the extreme case of IE ≈ EA (as for **1b**/**2d**), no optical transitions due to ionized molecules (indicative of integer-charge transfer) are observed, which fully supports the doping model described above.

Figure 2



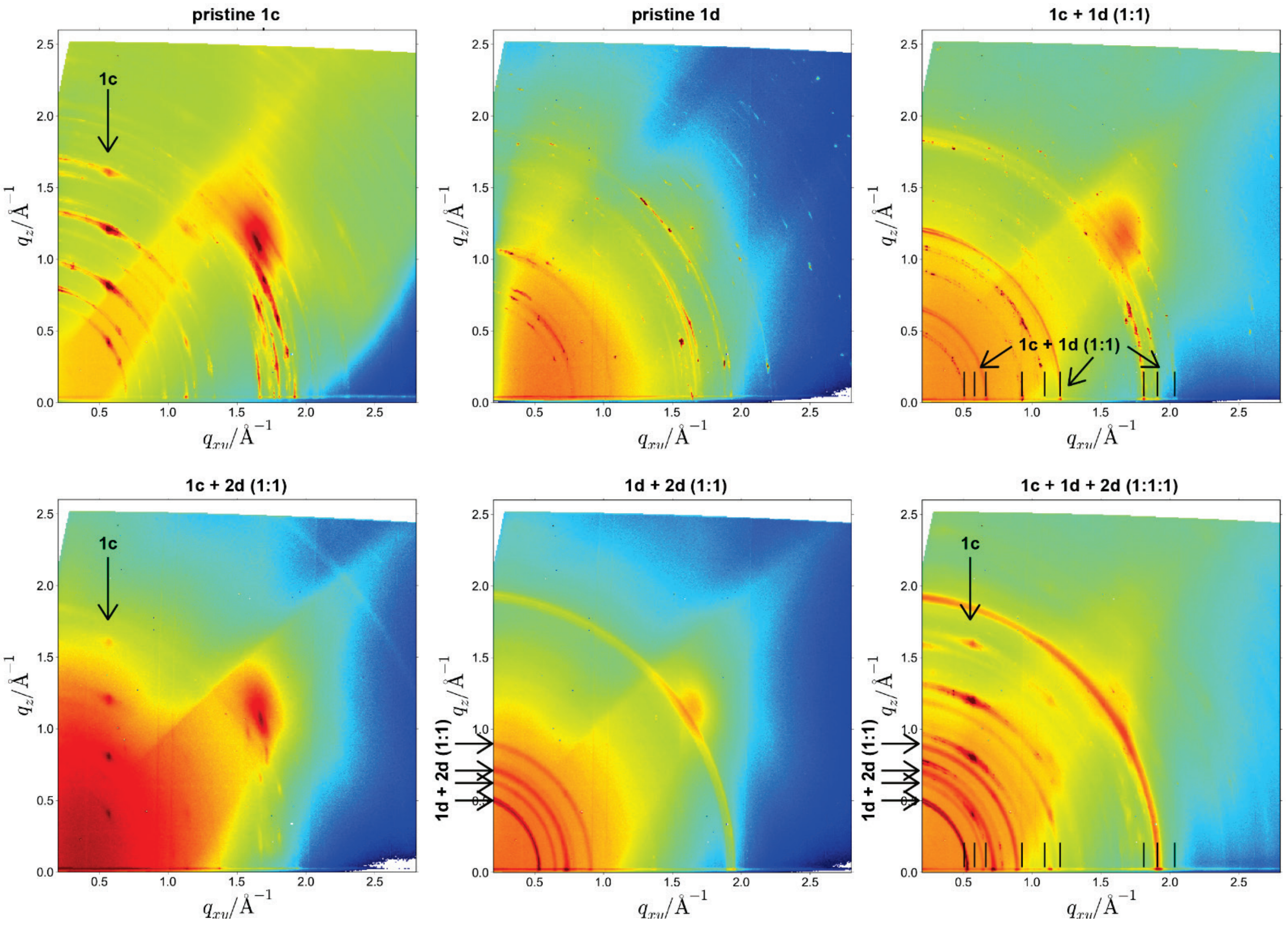
Via grazing incidence x-ray diffraction reciprocal space mapping (RSM) carried out at ESRF ID-10 we compared the structural arrangement in solution-processed *pristine* films of **1b** to that in 1:1 *mixed* films of **1b**+**2a** and **1b**+**2d**, as shown in Fig. 2. For the pristine film, (001)-textured growth (lattice spacing of d_{001} = 31.42 Å, as deduced from concomitant specular x-ray diffraction experiments) is observed in a structure similar to that of pure **1a** [3].

A refinement of simulated against experimental peak positions yields monoclinic unit-cell parameters of $a = 6.13$ Å, $b = 7.81$ Å, $c = 31.81$ Å, $\beta = 97.0°$ for **1b**. We note by the side that the unit-cell of an ultra-thin film (spin-coating speed 600 rpm instead of 300 rpm) is found to be slightly altered ($d_{001} = 30.73$ Å) to $a = 6.10$ Å, $b = 7.71$ Å, $c = 30.96$ Å, $\beta = 97.0°$, which points towards polymorphism mediated by the crystallization speed for this material [4]. Both 1:1 mixed-film samples exhibit an entirely altered crystalline structure (both: $d_{001} = 18.35$ Å), as already seen qualitatively from the highly different diffraction patterns in Fig. 2. However, the structure observed is independent from the strength of the dopant, as **1b**+**2a** and **1b**+**2d** turn out to be essentially isostructural via RSM. Importantly, no relevant contributions stemming from pure **1b** are observed, which clearly demonstrates mixed crystal growth of OSC and dopant in both cases. A comparison of the diffraction patterns to those of **1a**+**2a** and **1a**+**2d** (*cf.* Ref. [3]) reveals apparent similarities, which suggests that reducing the IE via oxygen incorporation into the molecular side-chains does not fundamentally impact the packing of the mixed-crystal structure; the precise refinement of the structure is currently in progress. Overall, above experiments show that, independent from the difference in energy between the OSC-IE and the dopant EA (that is, ≈ 0.8 eV for **1b**/**2a** down to ≈ 0 eV for **1b**/**2a**), a finite energy-level splitting remains in the supramolecular complex (as directly seen by the CPX transition T1 in optical spectroscopy). Because our RSM experiments evidence an identical molecular arrangement for the differently strong dopants, the degree of energy-level splitting can be disentangled from geometric influences, which would, themselves, impact the electronic coupling between OSC and dopant. In the present isostructural case, the change in energy-level splitting is, consequently, identified to be *solely* due to the different EAs of the dopants, while the transfer integral (β) stays essentially constant. Finally, this allows determining β to 0.47 eV via fitting T1 following a Hückel-like modelling, which will be subject of a forthcoming publication.

In a further set of experiments employing di-nitro- (strong acceptor) and di-amino-substituted (strong donor) benzothieno-benzothiophene derivatives **1c** and **1d**, respectively, we aimed to assess a *lower bound of the binding energy* of supramolecular complexes with dopants **2a**, **2b**, and **2d**; RSM data for a series with **2d** is exemplarily illustrated in Fig. 3. Pristine films of the OSCs **1c** and **1d** crystallize from solution in two different packing motifs easily discriminable through their specific RSM pattern, while RSM proves their 1:1 solution blend to form a mixed-crystal structure ("**1c + 1d (1:1)**") in the solid state ("fingerprint" reflections marked with vertical lines), as it might already be expected from their individual donor/acceptor character together with their similar molecular shape.

Upon admixture of the strongest p-dopant **2d** (i.e., a strong electron acceptor) to OSC **1c**, which, itself, exhibits acceptor character through its nitro-sidegroups, the resulting RSM pattern ("**1c + 2d (1:1)**") shows the same features as found in the pristine film of **1c** (marked with vertical arrows) and, hence, does not show indication for mixed-crystal formation. This situation changes completely for the OSC **1d** (donor character through its amino-sidegroups) and fully non-textured mixed crystal growth is observed by RSM ("**1d + 2d (1:1)**"); the characteristic "fingerprint" reflections are marked with horizontal arrows. Finally, an equimolar 1:1:1 blend of all three compounds ("**1c + 1d + 2d (1:1:1)**") shows a superposition of the RSM patterns of the pure acceptor-OSC **1c** and that of the **1d + 2d (1:1)** co-crystal, which indicates that the binding energy of the OSC/p-dopant complex is *larger* than that of the donor/acceptor co-crystal of the OSCs **1c** and **1d**.

Figure 3



Experimental

Measurements at ID-10 were carried out under Helium flux for sample protection using a three module PILATUS (DECTRIS) area detector for RSM and a point detector (scintillator counter) for specular x-ray diffraction. A high primary beam energy of 22 keV [beam geometry (v/h): 0.1/1 mm] was chosen in order to, (i), reduce potential degradation of the organic samples, and (ii), to capture the largest possible q-range ($\Delta q_{xy} \approx 3$ Å^{-1}, $\Delta q_z \approx 2.5$ Å^{-1}) at still reasonable resolution in RSM (incident angle of the primary beam: $\alpha_i = 0.064°$ for the SiOx substrates used). The “blind” regions (two vertical lines) of PILATUS due to the three individual modules of the detector were corrected through recording two images sufficiently shifted in q_{xy} direction by default; the individual maps were then joined by a custom-made script finally yielding the full RSM data (Figs. 2 and 3) and, furthermore, allowed to judge for sample degradation during the time of exposure to the primary beam (typically 60 sec). Transformation to reciprocal space was done using the software package x-ray utilities [5], which was adapted to the geometry of ID-10 in close cooperation with the authors.

References

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