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Energy-Level Alignment at Metal-Organic and Organic-Organic Interfaces in Bulk-Heterojunction Solar Cells

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Energy level alignment at metal-organic and organic-organic interfaces in bulk heterojunction solar cells

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Abstract—**Ultra violet photoelectron spectroscopy measurements in combination with the Integer Charge Transfer model is used to obtain the energy level alignment diagrams for two common types of bulk heterojunction solar cell devices based on poly(3-hexylthiophene) or poly(2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylene vinylene) as the donor polymer and (6,6)-phenyl-C61-butric-acid as the acceptor molecule. A ground state interface dipole at the donor/acceptor heterojunction is present for both systems but the origin of the interface dipole differs, quadrupole-induced in the case of poly(2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylene vinylene) and integer charge transfer state based for poly(3-hexylthiophene). The presence of bound electron-hole charge carriers (charge transfer states) and/or interface dipoles is expected to enhance exciton dissociation into free charge carriers, reducing the probability that the charges become trapped by Coulomb forces at the interface followed by recombination.**

Index Terms—**Interfaces, Photoelectron spectroscopy, Organic electronics, Solar cells**

I. INTRODUCTION

THE need for new energy sources that are renewable and have a small impact on the environment has caused a dramatic increase in both production of and research in photovoltaics in recent years. For example, production of photovoltaic-based energy sources has increased from less than 0.5 GW in 2000 to ~7.5 GW in 2008 [1]. Currently the leading technology in photovoltaic for solar energy conversion is silicon-based solar cells, but other thin film technologies such as CIGS and CdTe solar cells rapidly are increasing their market share and can achieve < 2Euro/Wp in panel production cost. Two of the key requirements for long term market success of solar energy conversion device solutions are (energy) cost-effectiveness and pollution-free environmentally friendly processing. The currently most widely used inorganic solar cell technologies involve fairly high energy consumption due to high temperature thin film or wafer growth and often contain both materials and processing steps that have a high negative impact on the environment.

An emerging technology that potentially can satisfy both requirements is the so-called organic-based bulk heterojunction solar cell [2,3]. Though the currently demonstrated power conversion efficiencies on the cell level are too low (7.9%, Solamer Energy Inc., certified by NREL December 2009) to compete with the established technologies, continued improvement combined with the low cost, low temperature processing that the technology offers through large area printing of the cells and modules could bring the organic solar cells into a Euro/Wp regime where they become competitive even for on-grid applications.

The concept of the bulk heterojunction solar cell is to create a network of donor-acceptor type organic-organic heterojunctions through blending of two (or more) organic components. The excitons created upon absorption of photons in such a film (by either the donor or acceptor molecules) are dissociated at the organic-organic heterojunctions into an electron-hole charge transfer state that eventually can become free negative and positive charge carriers and subsequently transported to the electrodes [3]. The energy level off-set at the heterojunctions should be large enough to overcome the exciton binding energy that typically is on the order of 500 meV in π-conjugated molecules [4,5]. However, if the off-set between the donor and acceptor levels is too large, substantial energy loss occurs and the overall power conversion efficiency of the cell will suffer [6]. The importance of the organic-organic heterojunction is further enforced by the recent results where weak ground state interactions between donor polymers and acceptor fullerenes leading to charge transfer (CT) complexes are shown to control the open circuit voltage, V_{oc}, of the cells [7-11].

Ultraviolet photoelectron spectroscopy (UPS) is an

excellent technique for measuring energy level off-sets at heterojunctions and the existence of ground state charge transfer complexes [12-14]. The so-called Integer Charge Transfer model [14-17] can be used in combination with UPS data to both analyze and predict energy level alignment and charge transfer at the type of weakly-interacting metal-organic and organic-organic interfaces that typically are present in bulk heterojunction solar cells [18,19]. Weakly interacting interfaces are characterized by a negligible hybridization of the π-electronic molecular orbitals and substrate wave functions, which is the case for organic-organic interfaces as well as metal-organic interfaces prepared under ambient atmosphere or low- to high-vacuum conditions [14]. Electron transfer across such interfaces can occur through tunneling when the substrate work function is higher (lower) than the formation energy of positively (negatively) charged states in the organic material. The energy of a positive integer charge transfer state, E_{ICT+}, is defined as the energy required to take away one electron from the molecule/polymer producing a fully relaxed state, *i.e.*, both electronic and geometrical relaxation are included as well as screening from the substrate, effect of intrinsic dipoles, etc. In an analogous manner, the energy of a negative integer charge transfer state, E_{ICT-}, is defined as the energy gained when one electron is added to the molecule/polymer producing a fully relaxed state. Hence, E_{ICT+} (E_{ICT-}) represent the lowest energy needed to oxidize (highest energy gained when reducing) a molecule/polymer located at the interface. The different basic regimes for energy level alignment in the ICT model can be described as follows:

$\Phi_{SUB} > E_{ICT+}$: Fermi level pinning to a positive integer charge transfer state, substrate-independent resulting work function $\Phi_{ORG/SUB}$.

$E_{ICT-} < \Phi_{SUB} < E_{ICT+}$: Vacuum level alignment, substrate-dependent resulting work function $\Phi_{ORG/SUB}$, slope = 1.

$\Phi_{SUB} < E_{ICT-}$: Fermi level pinning to a negative integer charge transfer state, substrate-independent resulting work function $\Phi_{ORG/SUB}$.

The existence of *e.g.* intrinsic dipoles [12,20] or quadrupoles [21,22] in the molecules/polymers add further complexity, modifying the $E_{ICT+,-}$ and/or introducing rigid shifts in the vacuum level alignment part of the $\Phi_{ORG/SUB}$ vs. Φ_{ORG} plot.

II. EXPERIMENTAL DETAILS

We have obtained the E_{ICT+} for regioregular poly(3-hexylthiophene) (P3HT) and poly(2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylene vinylene) (MDMO-PPV) as well as the E_{ICT-} for (6,6)-phenyl-C61-butric-acid (PCBM). The particular donor polymers and acceptor molecule are chosen as they have been widely used in bulk heterojunction solar cell studies [23]. UPS measurements were performed using monochromatized HeI radiation (hν = 21.2 eV) in a spectrometer of our own design and construction. The work function of the samples was derived from the position of the so-called secondary electron cut-off [14]. The measurements

sequence involved in obtaining the $E_{ICT+,-}$ values for the materials consisted of characterization of a series of passivated substrates spanning a wide range of work functions followed by spin-coating of the organic material and subsequent characterization of the coated substrate. Additional information on the technique can be found here [14,15]. The P3HT films were annealed *in situ* prior to UPS measurement to follow common practice in device fabrication [19,23]. The measurement error in the $E_{ICT+,-}$ values is estimated to be less than ±0.1 eV.

III. RESULTS AND DISCUSSION

In Fig. 1 is presented the work function measured before and after spin-coating of (a) PCBM, (b) P3HT and (c) MDMO-PPV films. For PCBM, the E_{ICT-} value is derived from Fig. 1a. Here, as PCBM is an electron acceptor, the low work function part of the plot is substrate independent (slope = 0), indicating that electronic charge is transferred from the substrate to the PCBM molecules at the interface until the resulting interface dipole brings the Fermi level into equilibrium with the fully relaxed singly occupied molecular orbital of PCBM⁻. The $\Phi_{ORG/SUB}$ energy is ~4.2 eV in this region, which then defines the E_{ICT-} value of PCBM, slightly smaller than the 4.3 eV value obtained in a previous study [19]. For Φ_{SUB} values higher than 4.2 eV, the plot becomes linear with slope = 1 as expected from the vacuum level alignment regime. An E_{ICT-} value of 4.2 eV means that when PCBM is brought in contact with a surface with a work function of less than 4.2 eV, spontaneous charge transfer will occur from the substrate to the PCBM, creating a dipole at the interface and pinning the Fermi level to 4.2 eV in the PCBM layer.

In Fig. 1b, the $\Phi_{ORG/SUB}$ vs. Φ_{ORG} plot for P3HT undergoes a transition from a slope = 1 at low substrate work functions to slope = 0 regime at higher substrate work functions as expected from the ICT model. The E_{ICT+} value derived from the plot is 4.0 eV (data originally obtained in ref. [15, 18]). An E_{ICT+} value of 4.0 eV means that when P3HT is brought in contact with a surface with a work function greater than 4.0 eV, spontaneous charge transfer will occur from P3HT to the substrate, creating a dipole at the interface and pinning the Fermi level to 4.0 eV in the P3HT layer.

For MDMO-PPV, see Fig. 1c, the $\Phi_{ORG/SUB}$ vs. Φ_{ORG} plot has a linear part with slope 1 for low substrate work functions and becomes substrate independent (slope = 0) at higher work functions with a fixed the $\Phi_{ORG/SUB}$ of 4.55 eV, which then is the E_{ICT+} value for MDMO-PPV. Note that there is a rigid off-set of ~0.3 eV downshifting the $\Phi_{ORG/SUB}$ vs. Φ_{ORG} values in the slope = 1 part of the plot compared to the vacuum level alignment regime typically seen for π-conjugated polymer deposited on passivated substrates [13]. Also, the spontaneous charge transfer and pinning to the E_{ICT+} level does not occur until the substrate work function is at least in excess of 4.7 eV (a straight line intercept between the slope = 1 and slope = 0 data yields ~4.8 eV), see Fig. 1c. This suggests the presence of

an interface dipole despite the absence of an integer charge transfer process. The origin of the interface dipole formation is not clear, but may be related to the co-planar conformation of the MDMO-PPV [24] and a preferential ordering in the spin-coated films with the polymer long axis in the plane of the substrate and the π-conjugated back bone lying face-on towards the substrate. MDMO-PPV is a π-conjugated polymer that has a co-planar conformation, *i.e.*, no significant ring torsion along the back bone. The π-orbitals have a node in the plane of the π-conjugated back bone and extend out of the plane on both sides of the phenyl and vinyl units. The positive charge of the nuclei remains in the plane, so a quadrupole is formed perpendicularly. (The σ-orbitals are in the plane of the back bone so they and their "corresponding" nuclear charge do not significantly contribute to the quadrupole). Seen from the perspective of the π-conjugated back bone, a dipole extends out in both directions with the negative sign on the outside of the plane. The energy required to remove an electron from the polymer will then depend on the direction: if it moves out perpendicular to the plane of the back bone it will have to overcome the dipole whereas if it moves in the plane it will experience no significant dipole affect, as demonstrated experimentally for planar π-conjugated molecules [21]. Drawn in an energy diagram, the molecular orbitals of the former case would experience a vacuum level shift increasing the energy needed to emit an electron as compared to the latter case, see Fig. 2. In practice, this leads to an increased ionization potential and electron affinity for transitions where the electrons exit/enter perpendicular to the back bone plane [21]. Furthermore, a discontinuity of the quadrupole field at an interface can induce a permanent interface dipole [22]. Such a discontinuity can be envisioned *e.g.* between a face-on lying MDMO-PPV layer and a substrate lacking a strong quadrupole, or between a face-on lying layer and edge-on lying layer of MDMO-PPV. If a quadrupole-induced dipole [21,22] at the substrate/MDMO-PPV interface is invoked, the ~0.3 eV off-set in the slope = 1 part of the plot and the ~0.3 eV extra "activation energy" needed to oxidize the MDMO-PPV at the interface can be reconciled. The scenario of a quadruple-induced dipole at the interface further implies that a similar dipole would form if a heterojunction if formed with MDMO-PPV as the substrate, but here the dipole would point in the opposite direction, which then produces an off-set that moves the slope = 1 part of the $\Phi_{ORG/SUB}$ vs. Φ_{ORG} plot *above* the Schottky-Mott line. This has been confirmed to be the case for MDMO-PPV/PCBM interfaces as we will show, but a more comprehensive study is needed to explore the validity of using quadrupoles and molecular order at MDMO-PPV interfaces to explain the effects seen.

An important consequence of the ICT model is that the energy level alignment at the weakly-interacting interfaces largely is determined by the $E_{ICT+,-}$ values, *i.e.*, the cost/gain of oxidizing/reducing a molecule residing at the interface. The $E_{ICT+,-}$ energies in essence samples the polaronic states of the π-conjugated systems that lies deepest in the gap as they

represent the most easily oxidized/reduced conformations at the interface, see Fig. 3 and ref. 14. These energies can then differ from the bulk values of the respective charge carrying species due to *e.g.* different inter- and intra-molecular order, different polarizability of the surrounding medium and of course Coulomb energy contribution from electron-hole coupling across the heterojunction as mentioned elsewhere [14].

Based on the ICT model and the $\Phi_{ORG/SUB}$ vs. Φ_{SUB} plots obtained for PCBM, P3HT and MDMO-PPV, we now derive the energy level alignment diagrams for two "classic" bulk heterojunction solar cells: ITO/PEDOT-PSS/MDMO-PPV:PCBM/Al and ITO/PEDOT-PSS/P3HT:PCBM/Al in order to obtain values of the internal electric fields and possible dipoles at the donor/acceptor interfaces. Both ITO and PEDOT can have a range of work functions based on batch and surface preparation [27-30], but here we use Φ_{SUB} =4.7 eV for ITO and Φ_{ORG} = 5.2 eV for PEDOT-PSS. The work function of metallic aluminum is ~4.1 eV. Note that LiF-modified Al contacts are often used for a variety of reasons and the resulting work function of LiF-modified Al can take a range of values depending on deposition order and materials involved [31-35]. In all cases, however, the resulting work function will be smaller than that for clean Al, and as we will show, from an interface energetics standpoint, the work function of clean Al already is low enough to pin the PCBM/Al contact.

The energy level alignment diagrams for a bulk heterojunction solar cell is not as straight forward as a bi-layer device. Due to the interpenetrating network consisting of the donor polymer and acceptor molecule, there are in fact many different pathways a charge can take travelling from one electrode to the other: a pure polymer path, a pure PCBM path, a first polymer then PCBM path, etc. As many of these pathways will not contribute significantly to the photovoltaic current in absence of an external bias, we will here limit the discussion to the "optimum" pathway for exciton dissociation and charge collection: ITO/PEDOT-PSS/MDMO-PPV/PCBM/Al and ITO/PEDOT-PSS/P3HT/PCBM/Al respectively, assuming electron collection at the Al contact and hole collection at the ITO contact.

In Fig. 4 is depicted the energy level diagram derived from the ICT model for the ITO/PEDOT-PSS/MDMO-PPV/PCBM/Al case (flat band condition). The ITO/PEDOT-PSS interface behaves as a metal/metal contact [36] with the resulting work function increasing from 4.7 eV to 5.2 eV with a 0.5 eV dipole shift of the vacuum level. Since the new work function is larger than the E_{ICT+} energy of MDMO-PPV, spontaneous charge transfer will occur from MDMO-PPV to PEDOT-PSS at the interface until equilibrium is reached. The Fermi level then will be pinned to 4.55 eV due to the interface dipole that down-shifts the vacuum level by 0.65 eV. The ITO/PEDOT-PSS/(monolayer)MDMO-PPV system thus acts as a 4.55 eV work function contact for the subsequent MDMO-PPV layers into the device. For organic

semiconducting molecules, there is Fermi level equilibrium even through multilayer stacks [37,38], so the Fermi level is situated at 4.55 eV on the MDMO-PPV side of the MDMO-PPV/PCBM heterojunction. Furthermore, if the quadrupole-induced dipole is invoked, we expect an up-shift of the work function upon deposition of PCBM onto MDMO-PPV, which was confirmed experimentally by UPS with a increase of the work function to ~4.8 eV (induced interface dipole of ~0.25 eV). The E_{ICT-} of PCBM is 4.2 eV so no spontaneous charge transfer leading to pinning of the Fermi level to the E_{ICT-} level will occur at this interface. Fermi level equilibrium then puts the Fermi level at 4.8 eV in the PCBM layer. At the PCBM/Al contact there will be spontaneous charge transfer and an interface dipole as the E_{ICT-} of PCBM is greater than the work function of Al, and the Fermi level is pinned to 4.2 eV at the PCBM-side of the interface. Note that reducing the effective work function of the Al contact by a LiF sandwich layer will not change this, only increase the interface dipole at the metal contact. The LiF layer can effect the contact in other ways, however, including preventing covalent bonding between Al and PCBM and possible defects resulting thereof [32-34].

The energy level diagram for the P3HT-based device obtained by applying the ICT model is presented in Fig. 5 (flat band condition) and is in excellent agreement with studies obtained on P3HT:PCBM blends on PEDOT-PSS and CsCO$_3$ contacts [19]. The work function of the PEDOT-PSS substrate is 5.2 eV and the E_{ICT+} of P3HT is smaller, 4.0 eV, so we expect spontaneous charge transfer at the interface from P3HT to PEDOT-PSS until equilibrium has been reached with the Fermi level becoming pinned to the E_{ICT+} value. The interface dipole created by the charge transfer is 1.2 eV and shifts the vacuum level down. Moving through the film until the heterojunction between P3HT/PCBM is reached, the Fermi level remains at 4.0 eV, as Fermi level equilibrium is maintained through the organic layers. The Φ_{SUB} is then 4.0 eV, smaller than the PCBM E_{ICT-} of 4.2 eV. The ICT model then predicts spontaneous charge transfer from P3HT to PCBM at the interface until equilibrium is reached with the Fermi level pinned to 4.2 eV. This introduces an interface dipole of 0.2 eV that shifts the vacuum level up. The Fermi level stays pinned at 4.2 eV in the PCBM layer until the PCBM/Al contact. Here there will be spontaneous charge transfer and an interface dipole as the E_{ICT-} of PCBM is greater than the work function of Al, and the Fermi level is pinned to 4.2 eV at the PCBM-side of the interface, just as for the MDMO-PPV based device.

The correlation of donor/acceptor levels and the open circuit voltage, V_{OC}, is not known at the present moment, though a great number of recent papers [3,7-11] have begun to shed light on the issue. It is already clear that V_{OC} is not equal to the donor HOMO and acceptor LUMO offset [9-11]. We propose that using the donor E_{ICT+} and acceptor E_{ICT-}, i.e., the actual oxidized and reduced singly occupied molecular orbitals rather than the neutral filled our empty HOMO and LUMO is more relevant to model the V_{OC}. The $E_{ICT+,-}$ levels obtained for

the interfaces determine the energy level alignment including dipoles, if any, at the interface but are not alone sufficient to model the V_{OC} as they represent the most strongly bound charged pairs at the interface, see Fig. 3 and ref. 14, and these levels are not expected to contribute to the current in the cell [3]. We speculate that in order to derive the V_{OC} one must in addition consider the integer charge carriers of the bulk material (bulk polarons), *i.e.*, the energy of the integer charge carriers when they have moved sufficiently far away from the interface to no longer be affected by the Coulomb interaction, as these states represent the charges that escapes the donor/acceptor heterojunction and are available to carry current through the device [3]. Such an approach will be pursued in future studies.

The energy level diagrams for the two bulk heterojunction solar cell devices shed some light on the exciton dissociation and charge collection properties. For both devices, there is a dipole at the donor/acceptor interfaces, with the negative side of the dipole pointing into the acceptor layer. A set of theoretical models have been presented [22,39] that shows that this type of interface dipole will enhance exciton dissociation into free charge carriers, significantly decreasing the chance that the electron- and hole states become trapped at the interface by Coulomb forces where they eventually would recombine resulting in a loss of photocurrent. The high efficiency seen in bulk heterojunction cells for these two polymer systems then likely can be attributed to the presence of the ground state interface dipoles (present in absence of illumination) that has the correct orientation. The interface dipole in the P3HT/PCBM case may have a further advantage in that it is created through the integer charge transfer process. The ICT model states that when $\Phi_{SUB} < E_{ICT-}$, spontaneous charge transfer occurs across the interface. For the ITO/PEDOT-PSS/P3HT/PCBM case this is reduced to E_{ICT+} (P3HT) $< E_{ICT-}$ (PCBM) which is satisfied as discussed earlier. Hence, at the interface, P3HT polymers will be oxidized forming p-polarons and on the PCBM side, PCBM molecules will be reduced forming n-polarons. Note that this process will sample the most easily oxidized polymer chains or chain segments on the P3HT side of the heterojunction, and the most easily reduced PCBM molecules at the other side, see Fig. 3. In this way, the most tightly bound charge transfer electron-hole pairs that can be created at the interface are already occupied in the (dark) ground state and are consequently not available to participate in the exciton dissociation process following a photon absorption event. This ensures that the charge transfer states formed immediately upon dissociation are slightly "hotter" than otherwise would be the case. Hot charge transfer states facilitate an increased chance of full separation and collection at the PEDOT-PSS and Al contacts according to theoretical predictions [3], so the P3HT:PCBM combination offers a further advantage in this regard.

IV. SUMMARY AND CONCLUSIONS

We have obtained the E_{ICT+} and E_{ICT-} values for materials

commonly used in bulk heterojunction solar cells and applied them in combination with the Integer Charge Transfer model to derive energy level alignment diagrams for MDMO-PPV:PCBM and P3HT:PCBM based bulk heterojunction solar cells. In both cases there are ground state interface dipoles at the organic-organic heterojunctions that will facilitate improved exciton dissociation and charge separation in the devices. We speculate that the P3HT:PCBM combination is particularly suitable as its interface dipole involves population of the most tightly bound charge transfer electron-hole pairs that can be created at the interface thus facilitating the creation of hotter (less tightly bound) charge transfer states upon exciton dissociation.

V. Acknowledgements

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Figure Captions

Fig. 1. UPS-derived $\Phi_{ORG/SUB}$ vs. Φ_{ORG} plots for (a) PCBM, (b) P3HT and (c) MDMO-PPV. A slope = 1 dotted line is added to illustrate the Schottky-Mott limit and a slope = 0 dotted line is added as a guide to the eye for the E_{ICT+} and E_{ICT-} values.

Fig. 2. Schematic picture of the quadrupole of a co-planar π-conjugated polymer segment with the positive charge in the plane and the negative charge located outside of the plane. The corresponding energy level diagram for an electron emitted parallel/anti-parallel to the normal of the π-conjugated plane is shown to the right of the picture.

Fig. 3. Energy level diagram of a π-conjugated molecule/polymer at an interface. The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of the neutral system are shown as solid black lines. The fully relaxed integer charge transfer states (polarons in the case of polymers) that are created upon oxidation or reduction of the molecule/polymer at the interface are drawn in the gap. Just as in the bulk of the organic films, the energy of charge carrying states formed upon oxidation/reduction will have a ~Gaussian distribution with a width (Δ, Δ' in the figure) that depends on inter- and intra-molecular order, ring torsion, local screening, etc. The highest lying oxidized state and the lowest lying reduced states at the interface define the position of the E_{ICT+} and E_{ICT-}, respectively.

Fig. 4. Energy level alignment diagram derived from UPS measurements and the ICT model for an ITO/PEDOT-PSS/MDMO-PPV/PCBM/Al pathway in a bulk heterojunction device. The diagram is drawn at flat band conditions and the work functions, $E_{ICT+,-}$ and organic-organic heterojunction dipole values are given in the figure.

Fig. 5. Energy level alignment diagram derived from UPS measurements and the ICT model for an ITO/PEDOT-PSS/P3HT/PCBM/Al pathway in a bulk heterojunction device. The diagram is drawn at flat band conditions and the work functions, $E_{ICT+,-}$ and organic-organic heterojunction dipole values are given in the figure.
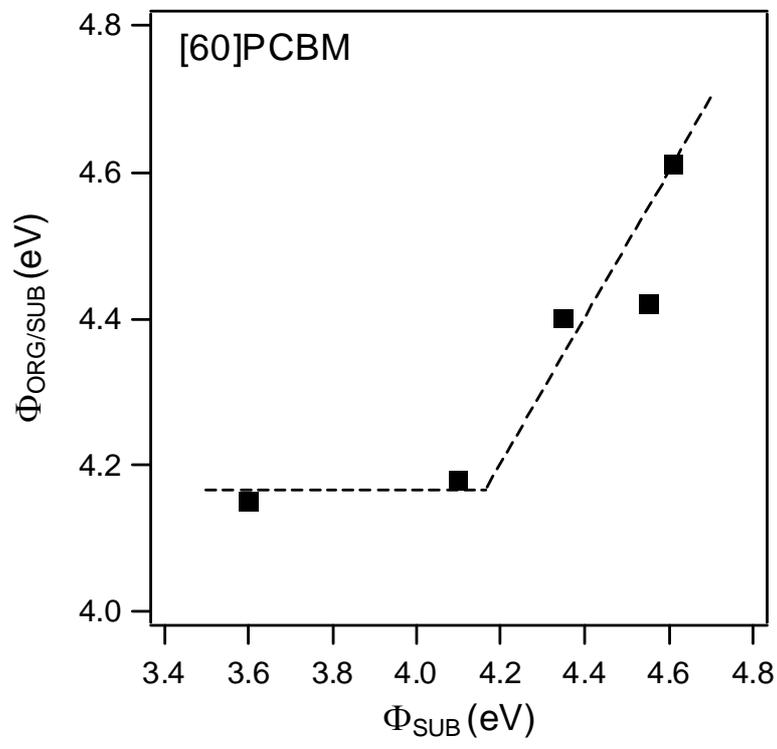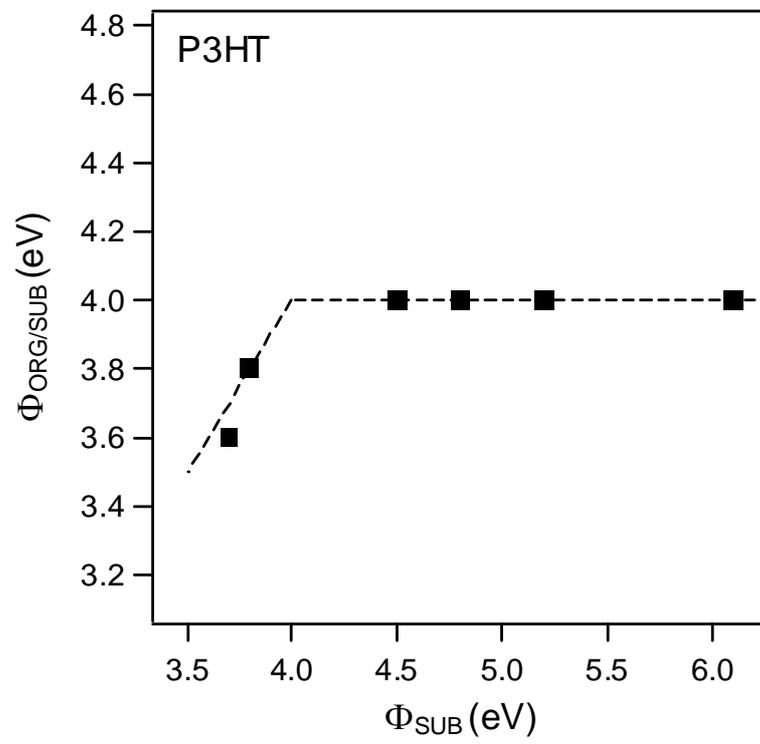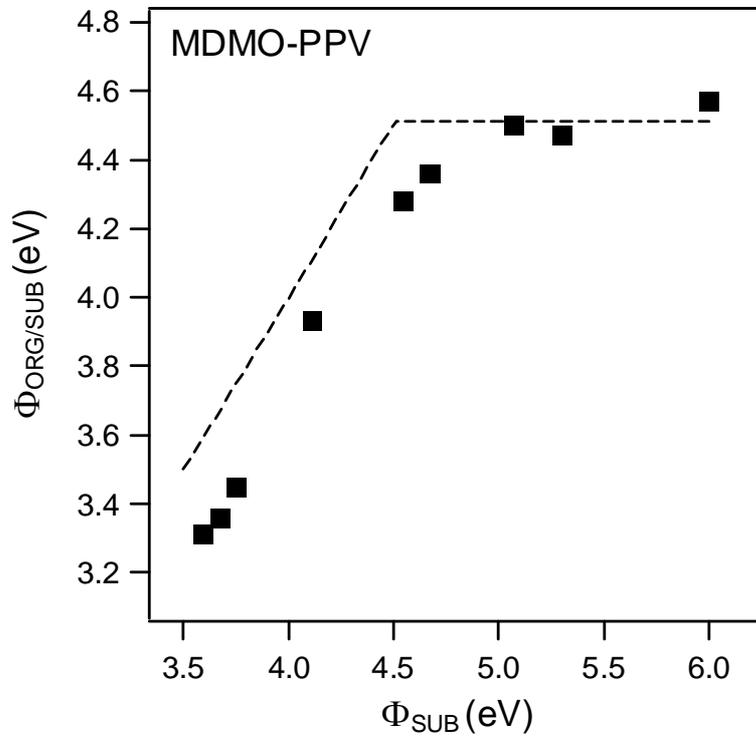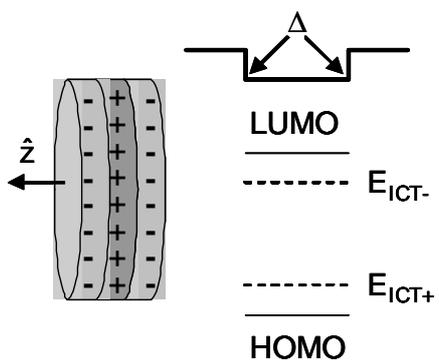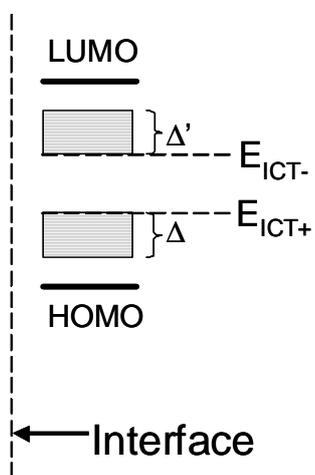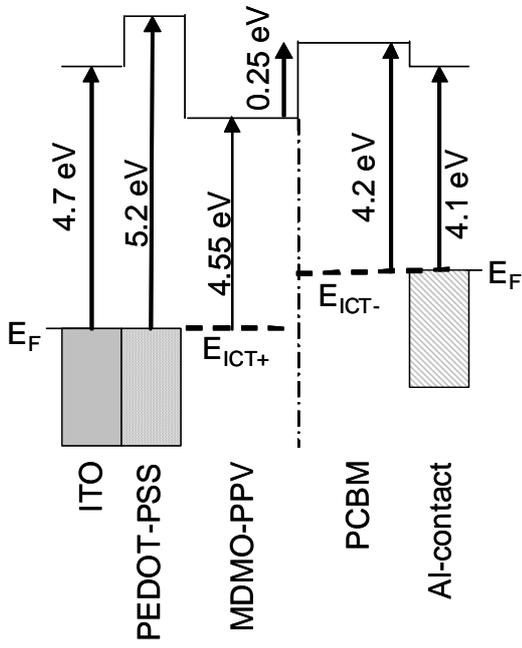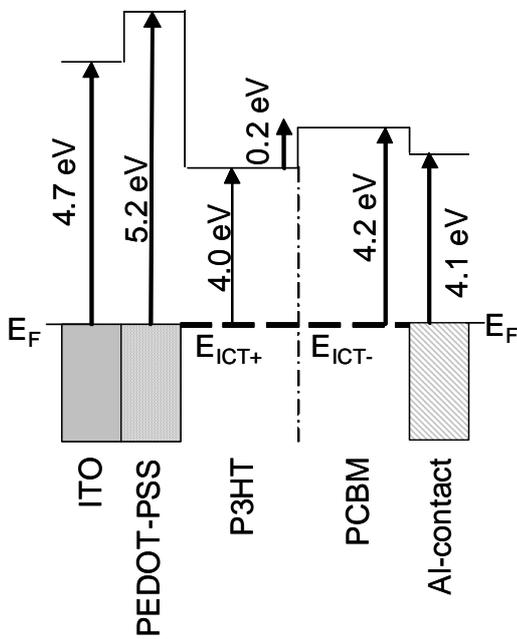
Figure 1a.

Figure 1b.

Figure 1c.

Figure 2.

Figure 3.

Figure 4.

Figure 5.