

Electrode-molecular semiconductor contacts: Work-function-dependent hole injection barriers versus Fermi-level pinning

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Contacts between two molecular organic semiconductors [*p*-sexiphenyl (6P) and pentacene] and conducting polymers (CPs) were investigated with photoemission spectroscopy. The dependence of the hole injection barrier (HIB) at 6P/CP interfaces on substrate work function (ϕ) exhibited a transition from almost Schottky-Mott limit-like behavior to Fermi-level pinning. For pentacene, no significant variation of the HIB as function of ϕ was observed, despite the large range of ϕ spanned by the CPs (4.4–5.9 eV). The results on contacts with CPs are compared to those with metals, where none of the two limiting cases for HIBs as a function of ϕ was observed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2364166]

One key issue for the commercialization of (opto)electronic devices based on organic semiconductors is the energy level alignment at contacts between electrodes and the organic material. In most devices charges have to be transported across such interfaces, and therefore low charge injection barriers are required. Therefore, a comprehensive understanding of the physicochemical mechanisms governing the energy level alignment at organic/electrode interfaces is elementary for further progress in the field, as documented by numerous publications.^{1–7} Conducting polymers based on polyethylenedioxythiophene (PEDT) and sulfonate moieties represent a promising class of materials for the use as anodes, in particular, in view of all-organic devices.^{8,9} In a recent report¹⁰ hole injection barriers (HIBs) between pentacene and different PEDT/sulfonate formulations were shown to be independent of very different initial conducting polymer (CP) work function (ϕ) values (ca. 4.3–5.2 eV). As a possible explanation, a charge-transfer-type reaction between pentacene and the CPs was proposed, leading to the observed Fermi-level pinning within the organic energy gap.¹⁰

In the present work we show that the results obtained for pentacene on PEDT/sulfonate-based electrodes cannot be readily generalized to other organic semiconductors. Using ultraviolet photoelectron spectroscopy (UPS), we find a significant dependence of HIBs on the initial polymer ϕ for the case of *p*-sexiphenyl (6P) deposited on PEDT/sulfonate polymers. This observation is explained by the larger ionization energy of 6P compared to that of pentacene, inhibiting a significant charge transfer between 6P and sulfonate moieties. These results are compared to conventional 6P/metal contacts. Furthermore, x-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition of the pristine CPs.

Two commercial PEDT/polystyrenesulfonate (PSS) dispersions with different PEDT:PSS ratios (in parentheses) were investigated, namely, Baytron® P AI4083 (1:6) and Baytron® P CH8000 (1:20). Thin films were prepared by spin casting the dispersions onto freshly cleaned and

UV/O₃-treated (30 min) indium tin oxide (ITO) (on glass) substrates in ambient. After heating the samples at ca. 200 °C for 5 min they were transferred into the ultrahigh vacuum system for photoemission experiments. The annealing step was omitted for one sample (CH8000-RT). A modification of PEDT with sulfonate groups attached via an alkoxy chain [PEDT-S (Ref. 11)], was also spin cast from aqueous solution onto ITO substrates and annealed before use. The *in situ* polymerized version of PEDT (IS-PEDT) was prepared as described elsewhere.¹⁰ Another CP that was used was a dispersion of PEDT, a sulfonic acid polymer derivative and a fluorinated sulfonic acid polymer¹² (PEDT/FP). The chemical structures of the polymers are shown in Fig. 1.

Photoemission experiments were performed at the end station SurfCat (Ref. 13) (beamline PM4) at the synchrotron

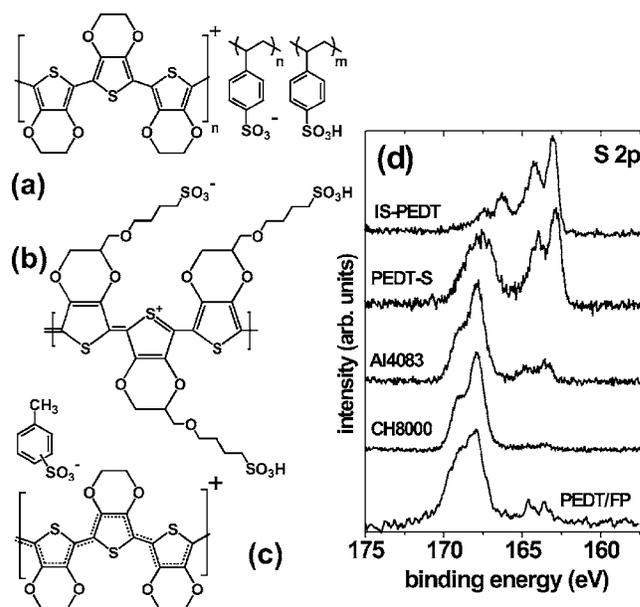


FIG. 1. Chemical structures of (a) PEDT/PSS, (b) PEDT-S, and (c) IS-PEDT. (d) S 2*p* core level spectra for the different conducting polymers.

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TABLE I. Comparison of experimental (expt.) and theoretically expected (theor.) stoichiometries of different PEDT/sulfonate ratios obtained from S 2*p* core level spectra (Fig. 1).

Sample	PEDT:sulfonate (expt.)	PEDT:sulfonate (theor.)
IS-PEDT	3:1	3:1
PEDT-S	1:1	1:1
AI4083	1:6	1:6
CH8000	1:24	1:20
PED/FP	1:8	...

light source BESSY GmbH (Berlin). The excitation energies for UPS and XPS were 35 and 630 eV, respectively. Photoemission spectra were collected with a hemispherical electron energy analyzer set to an energy resolution of 100 meV. In order to determine sample work function changes, the secondary electron cutoff was recorded with a -10 V sample bias.

p-sexiphenyl (Tokyo Kasei Kogyo, Co., Ltd.) and pentacene (Aldrich) were evaporated in the preparation chamber (base pressure $< 1 \times 10^{-7}$ mbar) from resistively heated pin-hole sources. The thin film mass thickness was monitored with a quartz crystal microbalance.

All CPs investigated in this study have in common that they are composed of PEDT and sulfonate moieties. The sulfur atoms contained in these moieties have different binding energies (BEs) of the S 2*p* core levels, which enables the determination of the surface PEDT:sulfonate ratio by XPS, since the elastic mean free path at the kinetic energy (here ca. 460 eV) of electrons ejected from the S 2*p* levels is about 0.8 nm.¹⁴ The S 2*p* core level spectra of each polymer exhibited two doublets (due to spin-orbit coupling), chemically shifted by ca. 4.5 eV BE [Fig. 1(d)]. According to earlier studies,¹⁵ the low BE doublet was assigned to sulfur in PEDT and the high BE doublet to the sulfonate. Small BE shifts between different CPs are attributed to slight changes in the exact chemical environment of sulfurs, since the chemical structures of the polymers differ to some extent [Figs. 1(a)–1(c)]. The PEDT:sulfonate ratio was determined by fitting the spectra with two doublets (mixed Lorentzian-Gaussian lineshape after Shirley-background subtraction) and calculating the area of each doublet (program WINSPEC, Namur University). The experimentally determined ratio was very close to the one expected for the bulk materials (see Table I). The deviation for CH8000 is considered to be within the experimental error because the S 2*p* intensity from PEDT is very low. Similar to earlier reports,¹⁰ the CPs exhibited very different work function values, spanning the range from ca. 4.4 eV (IS-PEDT) to ca. 5.25 eV (CH8000). Noteworthy is that CH8000-RT exhibited $\phi = 5.4$ eV, and the polymer mixture (PEDT/FP) an exceptionally high ϕ of 5.9 eV.

Stepwise increasing amounts of 6P (starting from submonolayer coverage up to ca. 12 nm mass thickness) were evaporated onto the different CPs, and photoemission spectra taken after each step. Throughout all deposition sequences the molecular levels stayed at the same BE, indicating flat-band conditions away from the interface.³ Representative UPS spectra of this series are shown in Fig. 2. In total, we observed a rigid shift of 6P valence features towards lower BE by 0.8 eV when changing from low- ϕ substrates

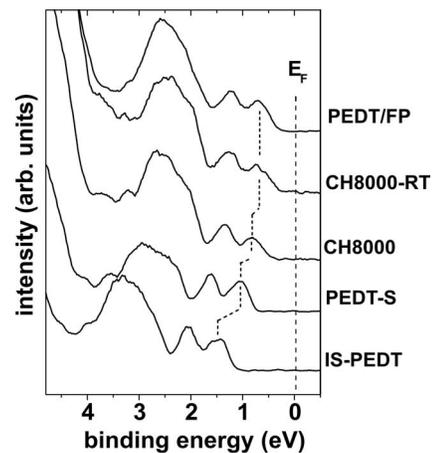


FIG. 2. UPS spectra of ca. 12 nm thick 6P films on different conducting polymers. The dashed line indicates the rigid shift, for example, of the HOMO level.

(IS-PEDT) to high- ϕ substrates (PEDT/FP). Accordingly, HIBs (defined as the energy difference between the low BE onset of emission from the highest occupied molecular orbital (HOMO) and the substrate Fermi level) changed from 1.15 eV (IS-PEDT) to 0.35 eV (PEDT/FP). Note that the change of the HIB (0.8 eV) did not parallel that of the substrate ϕ (1.5 eV).

HIB values for 6P on CP and metal substrates as function of pristine substrate ϕ are summarized in Fig. 3(a), together with sample vacuum level changes (Δ_{vac}), i.e., difference of sample ϕ before and after organic material deposition. Data points for 6P/metal interfaces could be fitted with one *S* parameter^{4,16} ($S = dE_F/d\phi_M$, where E_F denotes the position of the Fermi level in the organic material energy gap and ϕ_M the metal work function) over the entire ϕ range, yielding $S_{M,6P} = 0.51$ for HIB and a slope of $k_{M,6P} = 0.46$ for Δ_{vac} . The deviation of *S* from 1 (the value expected if the Schottky-Mott limit holds^{4,16}) for organic semiconductor/metal interfaces has been reported before.^{4,16} In general, *S* is not a molecule-specific parameter, rather it is determined by

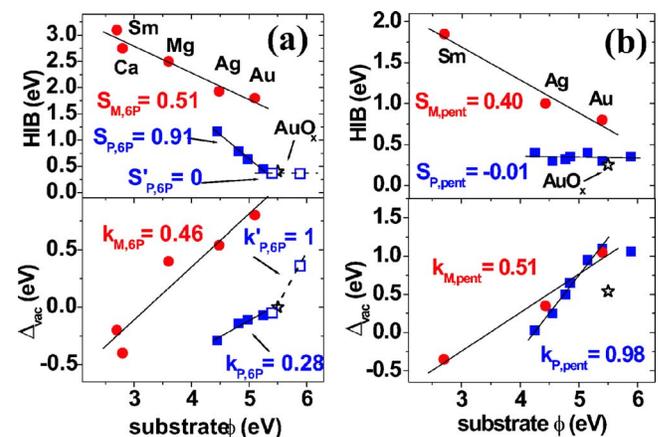


FIG. 3. (Color online) HIB and Δ_{vac} as a function of initial substrate ϕ (squares for conducting polymers and circles for metals) for (a) (6P) and (b) pentacene. 6P/metal data are from Sm (Ref. 20), Ca (Ref. 21), Mg (Ref. 22), Ag (Ref. 23), and Au (Ref. 3). Pentacene/metal and pentacene/CP (up to $\phi = 5.2$ eV) data are from Ref. 10. Filled squares in (a) correspond to the following CPs (for increasing ϕ): IS-PEDT, PEDT-S, AI4083, and CH8000. The open stars are data for molecules on AuO_x; the open squares in (a) are for 6P on CH8000-RT and PED/FP. (Dashed) lines are linear fits to the respective data points.

the specific interaction between the organic molecule and the substrate. The S parameter for 6P/CP interfaces ($S_{P,6P}$) cannot be fitted with one value over the entire investigated ϕ range [see Fig. 3(a)]. Apparently, the four low- ϕ data points yield $S_{P,6P}=0.91$ (and $k_{P,6P}=0.28$). Interestingly, this S value is very close to 1, i.e., the Schottky-Mott limit. Still, more work is required to understand why the sum of $S_{P,6P}$ and $k_{P,6P}$ deviates from a value of 1. Included in Fig. 3 are data points obtained for interfaces between the organic materials and Au that has been oxidized by UV/ozone treatment.¹⁷ Such Au surfaces exhibited ϕ values of 5.45 eV, i.e., between those of CH8000 and PEDT/FP. With this additional data point and the one obtained for 6P on CH8000-RT in Fig. 3(a), a transition from almost Schottky-Mott limit-like behavior to Fermi-level pinning is observed for interfaces with 6P at a critical ϕ between 5.25 and 5.40 eV. The dashed lines correspond to slopes of $S'_{P,6P}=0$ (and $k'_{P,6P}=1$). The transition supposedly occurs when the HIB becomes of the same magnitude as the positive polaron relaxation energy,⁷ which is derived from the present data to be 0.4 ± 0.1 eV for 6P. This value represents the *lowest possible HIB* for virtually any 6P/electrode interface in thermodynamic equilibrium, i.e., if charge exchange across the interface is possible. Note that due to the disparity of $S_{M,6P}$ and $S_{P,6P}$ it is impossible to relate the above-described transition for the behavior of S to the substrate work function. Instead, fundamentally different types of interactions between the organic semiconductor and metals and CPs govern interface energetics. This is still being debated at present.^{1-7,18} In particular, the mechanism of charge transfer at organic/CP interfaces needs to be explored in the future; for instance, Δ_{vac} even changes the sign for 6P and different CPs [Fig. 3(a)].

For comparison, according to experimental results for pentacene/electrode interfaces are compiled in Fig. 3(b), including additional data points for interfaces to oxidized Au (Ref. 17) and PEDT/FP (present study). While slopes for metal substrates $S_{M,\text{pent}}$ and $k_{M,\text{pent}}$ (Ref. 19) were rather similar to corresponding values obtained for 6P, Fermi-level pinning was observed for pentacene/CP interfaces for all ϕ values, i.e., $S_{P,\text{pent}}\approx 0$ and $k_{P,\text{pent}}\approx 1$. The reason for this is the smaller ionization energy of pentacene (ca. 4.9 eV) compared to that of 6P (ca. 5.8 eV). The polaron relaxation energy for pentacene extracted from Fig. 3(b) is 0.35 ± 0.1 eV. A direct charge-exchange reaction at 6P/CP interfaces (as proposed for pentacene/CP interfaces) is highly unlikely due to the high ionization energy of 6P.

In conclusion, photoemission spectroscopy was used to characterize interfaces between two molecular organic semiconductors (6P and pentacene) and (i) metals and (ii) conducting polymers based on PEDT and sulfonate. For both molecular materials S parameters for interfaces towards metals were found to be significantly lower than 1, i.e., 0.5 for 6P and 0.4 for pentacene. Contacts between 6P and CPs that had $\phi\leq 5.25$ eV exhibited S of almost 1. For substrates with $\phi\geq 5.4$ eV we found $S=0$, indicating that a transition from almost Schottky-Mott limit-like behavior to Fermi-level pin-

ning was observed for 6P. In contrast, contacts between pentacene and CPs exhibited Fermi-level pinning for all ϕ values, due to the ca. 1 eV smaller ionization energy of pentacene compared to that of 6P. Consequently, a lowest possible HIB may exist for every organic semiconductor, which can be achieved at a material-dependent critical substrate ϕ . Increasing ϕ above the critical value would not lead to a further decrease of the HIB.

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