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# **Energy level alignment regimes at hybrid organic–organic and inorganic–organic interfaces**

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## **Abstract**

Ultraviolet photoelectron spectroscopy has been used to determine the energy level alignment at interfaces of molecular hole-transporting materials and various conductive substrates. Depending on the work function of the substrate,  $\phi_s$ , a transition between two different energy level alignment regimes has been observed: namely vacuum level alignment and Fermi level pinning. The transition is associated with spontaneous positive charge transfer across the interface to the organic semiconductors above a certain material-specific threshold value of  $\phi_s$ . The charge transfer results in formation of an interfacial dipole of a magnitude that scales with  $\phi_s$ . In the vacuum level alignment regime, the hole-injection barriers scale linearly with  $\phi_s$ , while in the Fermi level pinning regime, these barriers are constant and independent of  $\phi_s$ .

## Introduction

Thin film architecture of organic light emitting diodes (OLEDs) encompasses multiple inorganic–organic and organic–organic junctions, the properties of which have a strong impact on device performance. For this reason, much of the effort in organic electronics has been focused on understanding and modification of the electronic properties of the interfaces [1-5]. The most common inorganic–organic interface is comprised of a conductive electrode and an organic hole (electron) transporting layer, often denoted as the HTL (ETL) [6]. At such interfaces, the magnitude of the barrier for charge injection depends on the energy level alignment between the Fermi level of the electrode and the highest (lowest) occupied (unoccupied) molecular orbital HOMO (LUMO) of the transport layer. Under the assumption of common vacuum levels (Schottky-Mott limit) the estimates of the hole-injection barrier  $E_V^F$  can be made when ionization potential (IP) of an HTL and the work function ( $\phi_s$ ) of an anode are known (see Fig. 1a). Often, due to formation of chemical bonds, charge transfer or a “push-

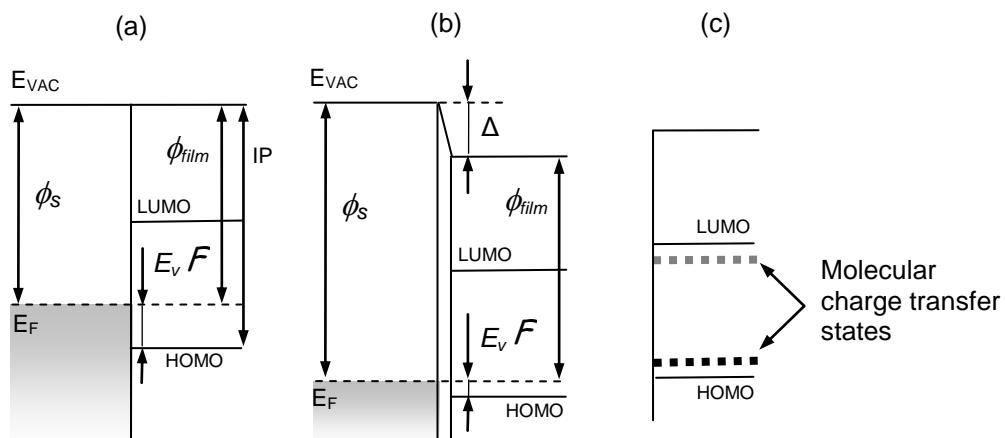


Fig. 1. Energy level diagram for interfaces of organic semiconductor and conducting substrate: (a) vacuum level alignment, (b) vacuum level shift and (c) molecular charge transfer states.

back” effect, the interfacial dipole is formed [1,2,5,7,8], which manifests itself as a vacuum level offset (denoted as  $\Delta$ ). This, in turn, negates the assumption inherent in the Schottky-Mott limit and affects  $E_V^F$  accordingly, thus determining the magnitude of  $\Delta$ ,

as shown in Fig. 1b. Therefore, in the process of developing OLEDs this effect must be taken into account.

The benefit of a good match between electrode work function  $\phi_s$  and the IP of an HTL may be hindered by a negative vacuum level shift that occurs at the corresponding interface. Such a shift pushes the occupied electronic levels away from the substrate Fermi level. This effect seems to be particularly significant for the interfaces with reactive or high work function, atomically clean metal surfaces, *i.e.*, metals with a large surface dipole contribution to the work function [7], [9,10]. Polymer-based high work function materials, such as the common electrically conducting polymer PEDOT-PSS [or poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid)], have been reported to lead towards more favorable energy level alignment with hole transporting materials [8,11]. However, significant vacuum level shifts, preventing reduction of hole-injection barrier, have been observed also for polymeric substrates [10].

To gain further understanding of this phenomenon, we have studied the energy level alignment at various interfaces of several common HTL materials and several organic and inorganic substrates. To keep consistency between the substrates, all of them were air exposed (not atomically clean), hence passivated by the presence of hydrocarbons.

The molecules chosen span a wide range of IP: CBP (*4,4'-N,N'-dicarbazolyl-biphenyl*), IP = 6.1 eV; NPB (*N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1-biphenyl-4,4-diamine*), IP = 5.35 eV; and *m*-MTDATA (*4,4,4''-tris[3-methyl-phenyl(phenyl)amino]-triphenylamine*), IP = 5.0 eV. The corresponding chemical

structures are depicted schematically in Fig. 2. A range of inorganic and organic materials was chosen for substrates to span wide variation of

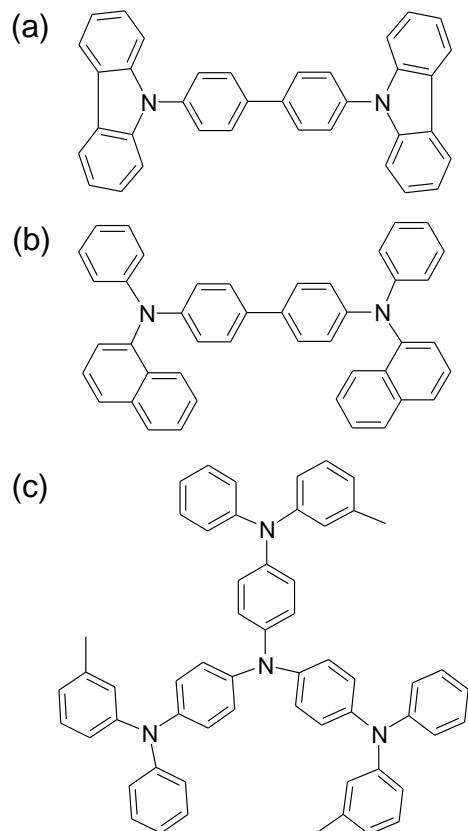


Fig. 2. Chemical structures of the organic molecules studied: (a) CBP, (b) NPB and (c) *m*-MTDATA.

work functions. In particular, a novel high work function polymer blend PEDOT-PFESA [or poly(3,4-ethylenedioxythiophene) poly(per-fluoroethylene sulfonic acid)] provides substrates with a work function as high as 5.8 eV [12]. Note, that the work function of PEDOT-PFESA exceeds the IPs of *m*-MTDATA and NPB, which, within Shottky-Mott limit, should correspond to barrier-less injection.

## Experimental

The various interfaces have been prepared *in situ* under ultra high vacuum (UHV) conditions by physical vapor deposition of the molecular materials. The molecules: CBP (99.9% purity), NPB (99.9% purity), *m*-MTDATA (99.9% purity) were prepared at DuPont. The molecules were evaporated from resistively heated glass Knudsen cell and condensed onto the substrates held at room temperature. The pressure in the vacuum chamber during the growth of the molecular films never exceeded  $3 \times 10^{-9}$  mbar. The deposition rate was set to approximately 3 Å/min, as calibrated from the attenuation of Au(4f) core level line of the substrate, measured by X-ray photoelectron spectroscopy (XPS). The following substrates were used in the study: (as-received) aluminum (with a thin native oxide),  $\phi_s = 3.75\text{--}3.85$  eV; silicon (with a thin native oxide),  $\phi_s = 4.0\text{--}4.1$  eV; and gold,  $\phi_s = 4.5$  eV; indium tin oxide  $\phi_s = 4.5$  (as-received) and cleaned in detergent (Neutracon), acetone and isopropanol,  $\phi_s = 4.8$  eV; PEDOT-PSS,  $\phi_s = 5.0\text{--}5.2$  eV [13]; and PEDOT-PFESA. In case of PEDOT-PFESA, the dispersions with pH = 5.2 and pH = 1.9 were used, which provided films with work functions of 5.4 eV and 5.8 eV, respectively. The water dispersions of the polymeric materials were obtained from Bayer and Dupont, respectively. The polymeric substrates were prepared by spin coating on ITO.

Ultraviolet photoelectron spectroscopy (UPS) was employed to examine the correlation between the substrate work function and the energy level alignment at the interfaces of HTL. This technique is especially suited for such studies, since it enables direct probing of the occupied valence electronic levels as well as the vacuum levels, and therefore also vacuum level shifts, upon forming the interface. The value of ionization potential (IP) is measured as the onset of HOMO edge versus vacuum level [14]. UPS measurements were performed using monochromatized HeI radiation ( $h\nu = 21.2$  eV) in

a spectrometer of our own design and construction [15]. The measurement sequence involved characterization of the bare substrates followed by stepwise deposition and characterization of molecular add-layers.

Hole-only devices were fabricated by thermal evaporation of organics and aluminum on patterned indium tin oxide (ITO) coated glass substrates. The ITO thickness is 1400 Å with a sheet resistance of 30 Ω/square. The ITO substrates were cleaned ultrasonically in aqueous detergent solution and rinsed with distilled water. They were subsequently cleaned ultrasonically in acetone, rinsed with isopropanol, and dried in a stream of nitrogen. Immediately before device fabrication the cleaned ITO substrates were treated with O<sub>2</sub> plasma for 3 min. After film deposition, the devices were encapsulated with a glass lid, sealed with epoxy in an argon-filled glove box. *I*–*V* curves of the encapsulated devices were measured with a Keithley Source Measure Unit.

## Results and discussion

Fig. 3 shows the dependence of the effective work function of the molecular organic layers ( $\phi_{\text{film}}$ ) as a function of the known work function of the substrates ( $\phi_s$ ), measured by UPS. For values of the substrate work function,  $\phi_s$ , that fall within the intrinsic HOMO–LUMO energy gap of the molecular film, the effective work function of the organic over layer,  $\phi_{\text{film}}$ , follows the work function of the substrate (Schottky-Mott limit). The so-called interface slope parameter  $S=d(E_V^F)/d(\phi_s)$  [16], which is often used to characterize the energy level alignment at the interface, is then unity. The hole-injection barrier follows the changes in the substrate work function. However, when the Fermi level of the substrate approaches energy of HOMO, charge transfer across the interface results in formation of interfacial dipole  $\Delta$ . In turn, further increase in  $\phi_s$  does not affect  $\phi_{\text{film}}$ , instead stronger interfacial dipole is formed. Consequently, the barrier  $E_V^F$  remains constant with respect to  $\phi_s$  (slope parameter  $S = 0$ ) and the Fermi level of the substrate remains within the HOMO–LUMO energy gap. Actually, the Fermi level is pinned at a charge transfer state that lies in the vicinity of HOMO energy, as illustrated in Fig. 1c. Note that these charge transfer states would be equivalent to so-

called polaronic states in conjugated polymers [17]. The details of the observation that lead to the picture discussed in the paragraph above are presented below.

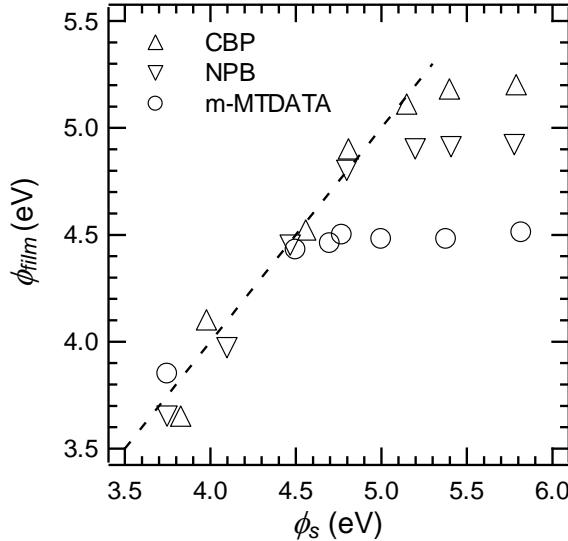


Fig. 3. The work function of the molecular organic layers ( $\phi_{film}$ ) versus the work function of the substrates ( $\phi_s$ ).

As shown in Fig. 4, a substantial reduction in the energy difference between the HOMO of NPB and the Fermi level of the substrate is observed for increasing  $\phi_s$ . The barrier for hole-injection decreases from 1.75 eV in the case of  $\text{Al}_x\text{O}_y$  ( $\phi_s = 3.75$  eV) down to 0.5 eV for ITO ( $\phi_s = 4.8$  eV). Within the substrate work function range from 3.75 eV to 4.8 eV, interfaces follow Schottky-Mott limit. The observed energy level alignment indicates a lack of significant interactions at the corresponding interfaces, and is likely related to the inert character of the surfaces of the substrates. This is in apparent contrast to the atomically clean metallic substrates. As reported by Koch et al. [8], deposition of NPB on sputtered-cleaned gold ( $\phi_s = 5.1$  eV) results in a negative vacuum level shift of 1.15 eV, and the formation of a hole-injection barrier as large as 1.4 eV. In the case of the NPB/gold interface reported here, no offset in vacuum level is measured, and the hole-injection barrier of 0.9 eV is significantly smaller than that for atomically clean gold. This is in agreement with the recent study by Wan et al. who reported that the

contaminated Au substrate with work function ( $\phi_s = 4.7$  eV) gives lower injection barrier than the atomically clean Au substrate. The reason for these differences lies in presence of the thin (0.5–1 ML) layer of hydrocarbons on the surface [18], which decreases surface-dipole contribution to the work function of the gold substrate [7]. For such substrate the tail of electrons spilling out from the metal surface into the vacuum is minimized. The important implications are as follows: (i) the initial work function of the substrate  $\phi_s$  is lower (with respect to atomically clean substrate) and corresponds predominantly to the bulk contribution; (ii) the push-back effect is not significant when the film of the organic semiconductor is present, since there is very little (if any) surface contribution to the  $\phi_s$ . Note that these results are important in device fabrication where physical vapour deposition (PVD) is not done under UHV conditions.

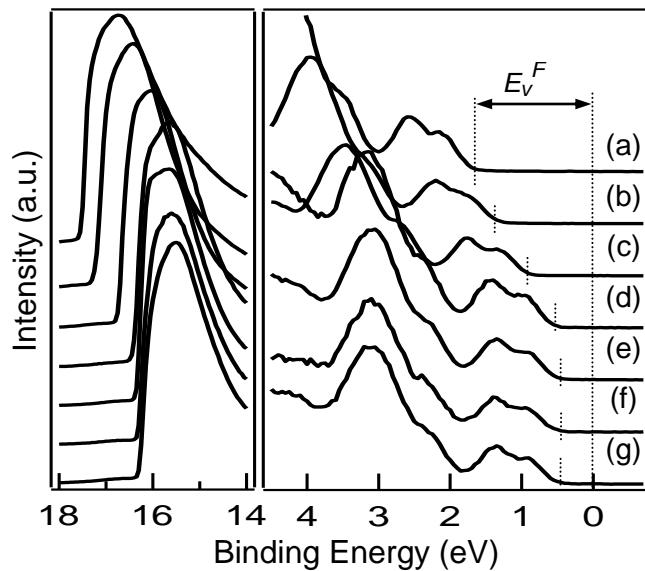


Fig. 4. UPS spectra of thin film of NPB deposited on: (a) aluminum/aluminum oxide –  $\phi_s = 3.75$  eV, (b) silicon/silicon oxide –  $\phi_s = 4.1$  eV, (c) gold –  $\phi_s = 4.5$  eV, (d) ITO –  $\phi_s = 4.8$  eV, (e) PEDOT-PSS –  $\phi_s = 5.2$  eV, (f) PEDOT-PFESA –  $\phi_s = 5.4$  eV, (g) PEDOT-PFESA –  $\phi_s = 5.8$  eV. The spectra are referred to the Fermi level of spectrometer at zero binding energy. Hole-injection barrier  $E_V^F$  is schematically drawn as the gap between the Fermi level and the leading edge of HOMO.

Within the Schottky-Mott limit, a further increase of the work function of the substrates would lead to further improvement in hole-injection. However, for NPB on PEDOT-PSS ( $\phi_s = 5.2$  eV), a substantial deviation from Schottky-Mott limit occurs. In this case, a downward vacuum level shift of 0.3 eV is observed. The hole-injection barrier height changes with respect to that of ITO only by 0.1 eV and is equal to 0.4 eV. This value agrees well with results reported earlier [8]. For large  $\phi_s$ , the magnitude of  $\Delta$  increases with increasing  $\phi_s$  of the substrates. For interfaces of NPB and PEDOT-PFESA ( $\phi_s = 5.4$  eV and 5.8 eV), the values of  $\Delta$  are  $-0.5$  eV and  $-0.9$  eV, respectively.

Meanwhile, HOMO onset stays pinned at the constant distance of about 0.4 eV from the Fermi level, as shown in Fig. 4. In this range of work functions the slope parameter  $S$  abruptly changes from unity to zero. The threshold value of  $\phi_s$ , which separates region of so called Fermi level pinning from that of Schottky-Mott limit, is found at about 4.9 eV.

This conclusion is consistent with the  $I$ - $V$  data from hole-only devices. We compared the injected current from ITO and PEDOT-PFESA substrates to NPB using the following hole-only devices: (a) ITO/NPB(200 nm)/Al(100 nm); and (b) ITO/PEDOT-PFESA(50 nm)/NPB(200 nm)/Al(100 nm). In these devices, electron injection from Al to NPB is not feasible due to the high barrier (Al work function – 4.0–4.5 eV; NPB LUMO – 1.4 eV) [19]. The work function for oxygen plasma cleaned ITO is nominally about 4.8 eV. PEDOT-PFESA with a work function of 5.4 eV was deposited by spin-coating, dried, and then moved into vacuum chamber for NPB deposition. The  $I$ - $V$  curves for these samples are shown in Fig. 5. We observed only slightly more current injected from PEDOT-PFESA to NPB in spite of its higher work function of 5.4 eV. Based on the HOMO value of 5.35 eV for NPB, we expect ohmic injection from PEDOT-PFESA to NPB. In this regime, the space-charge-limited current ( $J_{SCLC}$ ) obeys the Mott-Gurney equation,  $J_{SCLC} = (9/8)\varepsilon\varepsilon_0\mu V^2/d^3$ , where  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the vacuum permittivity,  $\mu$  is the carrier mobility,  $V$  is the applied voltage, and  $d$  is the device thickness. At field strength of  $4 \times 10^5$  V/cm (8 V), taking the mobility of NPB to be  $4 \times 10^{-3}$  cm<sup>2</sup>/(V s) (the average of literature reported values [20] and [21]), dielectric constant to be 3 (typical range for organic is 3–10),  $J_{SCLC}$  should be about 10 A/cm<sup>2</sup>. The observed current density of PEDOT-PFESA/NPB is only 0.11 A/cm<sup>2</sup>, which is about two orders-of-magnitude smaller than the expected space-charged-limited current

if injection were ohmic. This result is consistent with the conclusion of UPS study, that the hole-injection barrier at PEDOT-PFESA/NPB interface decreases only slightly ( $\sim 0.1$  eV) with respect to that of ITO/NPB (from 0.5 eV to 0.4 eV). For a purely injection-limited current, a 0.1 eV reduction in barrier would cause  $\sim 50$  fold increase in current which is not what we observed in Fig. 5. The current injection from ITO and PEDOT-PFESA to NPB therefore lies between the two extremes of space-charge-limited current and injection-limited current.

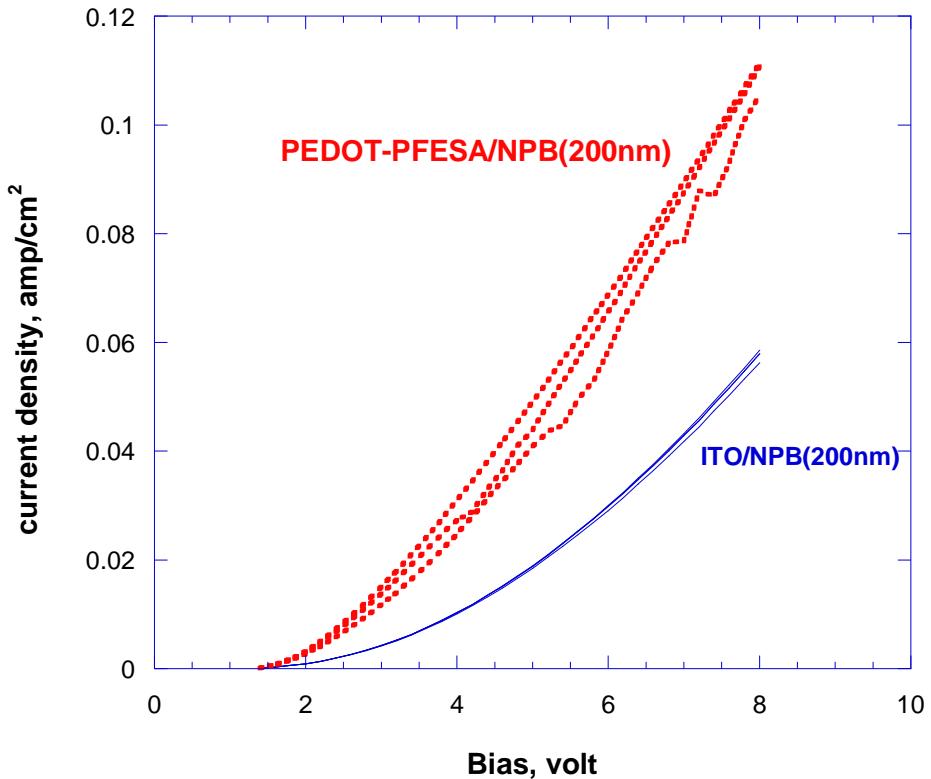


Fig. 5. Hole-only current–voltage curves of two types of devices: solid curves – ITO/NPB(200 nm)/Al(100 nm); dotted curves – ITO/PEDOT-PFESA(50 nm)/NPB(200 nm) /Al(100 nm).

Similar to the case of NPB, two distinct energy level alignment regimes are observed for CBP (see Fig. 3.). The vacuum level of the molecular film coincides with that of the

substrate (Schottky-Mott limit) for  $\phi_s$  smaller than approximately 5.2 eV. Within this regime, the hole-injection barrier  $E_V^F$  decreases from 2.3 eV to 0.9 eV, as the  $\phi_s$  is changed from 3.82 eV to 5.15 eV. On the other hand, for both PEDOT-PFESA high work function substrates, the barrier decreases only by about 0.1 eV, despite the work function increase by 0.2 eV and 0.6 eV, as compared to threshold value of 5.2 eV.

The energy level alignment of *m*-MTDATA follows the patterns seen for NPB and CBP. The threshold work function value above which significant interfacial dipole starts to form is at about 4.5 eV. Above this threshold the interfacial dipole scales directly with increasing  $\phi_s$  while the barrier for hole-injection stays constant at about 0.4 eV. Note that for *m*-MTDATA and PEDOT-PFESA ( $\phi_s = 5.8$  eV) interface, a downward vacuum level shift as large as 1.3 eV is observed. In the early stages of deposition there is broadening of the photoemission features of *m*-MTDATA located in the low binding energy region. This observation is tentatively interpreted as a result of charge transfer and presence of destabilized HOMO states in the spectrum. However, for low coverages, a signal from the substrate is also present and contributes to the background of the above-mentioned spectra. The overlap of the intensities from the substrate and the monolayer (or sub-monolayer) of the molecular film makes interpretation of broadening in molecular features, somewhat uncertain.

Recent study by Tsang et al. shows that the change of the electrode from ITO to PEDOT-PSS in the device with *m*-MTDATA as hole-transporting layer does not improve hole-injection. At the same time clear improvement is observed for NPB-based devices [22]. This can be explained by the results shown in Fig. 3. Both ITO/*m*-MTDATA and PEDOT-PSS/*m*-MTDATA interfaces fall into Fermi level pinning regime, therefore no improvement in hole-injection is expected. In contrast ITO/NPB interface is in vacuum level alignment regime, while the exchange of electrode to that of PEDOT-PSS results in Fermi level pinning and reduction of the hole-injection barrier across the interface. In other words, the Fermi level pinning regime should correspond to the lowest charge injection barrier (in terms of electronic level alignment) for a given molecular material.

The cases discussed above show clearly that there exist two types of different energy level alignment regimes at the interfaces of HTL and conducting substrates. Negligible

vacuum level shifts indicate that, up to a certain threshold  $\phi_s$  value, the interfaces in question exhibit essentially pure Schottky-Mott behavior, *i.e.*,  $S = 1$ . As a consequence, the barriers for hole-injection scale linearly with  $\phi_s$ . However, for  $\phi_s$  greater than the threshold value, the Fermi level of the substrate is pinned at a charge transfer level of the molecule. Since the charge-transfer state lies in vicinity of HOMO, the magnitude of the threshold value, above which pinning occurs, is higher for the molecules with higher IP.

Observed pinning causes formation of substantial interface charge-transfer dipole. The magnitude of the dipole scales linearly with  $\phi_s$ , while at the same time the barriers for hole-injection remain constant. In other words, by changing  $\phi_s$  the hole-injection barrier can be tuned only to certain value. Any further increase in  $\phi_s$  has little (if any) effect on the charge injection barrier, but results instead in an interfacial dipole layer.

Recently, similar results were reported for interfaces of semiconducting polymers spincoated onto a wide range of organic and inorganic substrates [4]. The effects of interfacial charge transfer have been discussed theoretically earlier [23]. The present results are consistent with these earlier predictions. A model of energy level alignment at the “atomically clean” metal–organic and organic–organic interfaces was recently proposed, where the interfacial electronic structure was interpreted in terms of an induced density of interface states (IDIS) [24] and [25]. For the interfaces of passivated substrates and molecular semiconductors, discussed in this work, the IDIS model does not appear to apply. This can be seen from abrupt change of the slope parameter,  $S$ , from 1 to 0 at the transition from vacuum level alignment to Fermi level pinning, when the work function of the substrate exceeds a certain material specific threshold value. In terms of density of states our experiments point to a model where the density of states in the semiconductor band gap peaks at the molecular charge transfer states, but is negligible elsewhere in the gap. Furthermore, for the substrate work function ranging from 4.8 eV to 5.2 eV (see Fig. 3) the formation of either large interfacial dipoles or lack thereof is observed, depending on the molecular semiconductor. Within IDIS model such behaviour of interfaces requires very different strength of the electronic coupling between Fermi states of the same substrate and different molecular semiconductors [18].

The IDIS model has already been considered in the study of the interfaces prepared by *in situ* deposition of TCNQ and TTF. In both cases Fermi level pinning was observed and proposed to originate from a charge exchange between the molecular film and the substrates [26].

## Summary

Ultraviolet photoelectron spectroscopy has been used to reveal the energy level alignment at the interfaces of molecular organic semiconductors, specifically NPB, CBP and *m*-MTDATA, and various conductive (passivated, not atomically clean) substrates with wide span of the work functions (3.75–5.8 eV). We have consistently observed a transition between two regimes of energy level alignment, namely vacuum level alignment and Fermi level pinning. The later regime results in the interfacial dipole that scales linearly with the work function of the substrate. Formation of this dipole is associated with spontaneous positive charge transfer across the interface to the molecular charge transfer states of the organic semiconductors. Within the Fermi level pinning regime, the barriers for charge injection are independent of the work function of the substrate, while within the vacuum level alignment regime, the barriers follow Schottky-Mott limit behavior, *i.e.*, they scale linearly with the work function of the substrate. These results show that the hole-injection barriers can be reduced by increasing the work function of the substrate only within certain limits. When the work function of the substrate exceeds the binding energy of the molecular charge transfer states, an interfacial dipole is formed, which inhibits the potential benefit of a high work function electrode.

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## References

- [1] H. Ishii, K. Sugiyama, E. Ito and K. Seki, *Adv. Mater.* **11** (1999), p. 605.
- [2] I.G. Hill, D. Milliron, J. Schwartz and A. Kahn, *Appl. Surf. Sci.* **166** (2000), p. 354.
- [3] W.R. Salaneck, K. Seki, A. Kahn and J.-J. Pireaux, *Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and Optoelectronic Applications*, Marcel Dekker, New York (2002).
- [4] C. Tengstedt, W. Osikowicz, W.R. Salaneck, I.D. Parker, C.-H. Hsu and M. Fahlman, *Appl. Phys. Lett.* **88** (2006), p. 053502.
- [5] A. Kahn, N. Koch and W. Gao, *J. Polym. Sci. Polym. Phys.* **41** (2003), p. 2529.
- [6] C.W. Tang, S.A. VanSlyke and C.H. Chen, *J. Appl. Phys.* **65** (1989), p. 3610.
- [7] X. Crispin, V. Geskin, A. Crispin, J. Cornil, R. Lazzaroni, W.R. Salaneck and J.-L. Brédas, *J. Am. Chem. Soc.* **124** (2002), p. 8131.
- [8] N. Koch, A. Kahn, J. Ghijsen, J.-J. Pireaux, J. Schwartz, R.L. Johnson and A. Elschner, *Appl. Phys. Lett.* **82** (2003), p. 70.
- [9] I.G. Hill, A. Rajagopal and A. Kahn, *J. Appl. Phys.* **84** (1998), p. 3236.
- [10] N. Koch, A. Elschner, R.L. Johnson and J.P. Rabe, *Appl. Surf. Sci.* **244** (2005), p. 593.
- [11] A.J. Mäkinen, I.G. Hill, R. Shashidhar, N. Nikolov and Z.H. Kafafi, *Appl. Phys. Lett.* **79** (2001), p. 557.
- [12] C. Tengstedt, A. Kanciurzewska, M.P. de Jong, S. Braun, W.R. Salaneck and M. Fahlman, *Thin Solid Films* **515** (2006), p. 2085.
- [13] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J.R. Reynolds, *Adv. Mater.* **12** (2000), p. 481.
- [14] W.R. Salaneck, S. Strafström and J.L. Brédas, *Conjugated Polymer Surfaces and Interfaces: Electronic and Chemical Structure of Interfaces for Polymer Light Emitting Devices*, Cambridge University Press, Cambridge (1996).
- [15] W.R. Salaneck, R. Bergman, J.-E. Sundgren, A. Rockett, T. Motooka and J.E. Greene, *Surf. Sci.* **198** (1988), p. 461.

- [16] K. Seki, E. Ito and H. Ishii, *Synth. Met.* **91** (1997), p. 137.
- [17] W.R. Salaneck, R.H. Friend and J.L. Brédas, *Phys. Rep.* **319** (1998), p. 231.
- [18] A. Wan, J. Hwang, F. Amy and A. Kahn, *Org. Electron.* **6** (2005), p. 47.
- [19] T. Schwieger, M. Knupfer, W. Gao and A. Kahn, *Appl. Phys. Lett.* **83** (2003), p. 500.
- [20] P.M. Borsenberger, E.H. Magin and J. Shi, *Physica B: Condens. Mat.* **217** (1996), p. 212.
- [21] Z. Deng, S.T. Lee, D.P. Webb, Y.C. Chan and W.A. Gambling, *Synth. Met.* **107** (1999), p. 107.
- [22] S.W. Tsang, S.C. Tse, K.L. Tong, S.K. So, *Org. Electron.*, in press,  
doi:10.1016/j.orgel.2006.06.002.
- [23] P.S. Davids, A. Saxena and D.L. Smith, *Phys. Rev. B* **53** (1996), p. 4823.
- [24] H. Vázquez, F. Flores, R. Osztwaldowski, J. Ortega, R. Perez and A. Kahn, *Appl. Surf. Sci.* **234** (2004), p. 107.
- [25] H. Vázquez, W. Gao, F. Flores and A. Kahn, *Phys. Rev. B* **71** (2005), p. 041306.
- [26] R.J. Murdey and W.R. Salaneck, *Jpn. J. Appl. Phys.* **44** (2005), p. 3751.