

Conjugated organic molecules on metal versus polymer electrodes: Demonstration of a key energy level alignment mechanism

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Ultraviolet photoemission spectroscopy is used to determine the energy level alignment at interfaces between three electroactive conjugated organic molecular materials, i.e., *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1-biphenyl-4,4'-diamine; *para*-sexiphenyl; pentacene, and two high work function electrode materials, i.e., gold and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate). Although both electrode surfaces have a similar work function (~ 5 eV), the hole injection barrier and the interfacial dipole barrier are found to be significantly smaller for all the interfaces formed on the polymer as compared to the metal. This important and very general result is linked to one of the basic mechanisms that control molecular level alignment at interfaces with metals, i.e., the reduction of the electronic surface dipole contribution to the metal work function by adsorbed molecules. © 2003 American Institute of Physics. [DOI: 10.1063/1.1532102]

Considerable research efforts are presently directed toward the realization of new organic-based electronic and optoelectronic devices. One of the most important factors that determine device function and performance is charge carrier injection from electrodes into the organic material. For hole injection, high work function electrodes, like oxygen-plasma treated indium tin oxide (ITO) or thin metal layers (Au and Pt) deposited on transparent substrates, are generally used. An organic alternative to these inorganic electrodes is the highly conductive polymer poly(3,4-ethylenedioxy thiophene)/poly(styrenesulfonate) (PEDT/PSS), which has a work function (ϕ) of ~ 5 eV (Ref. 1) and exhibits good optical, electrical, and processing characteristics.

From the view point of investigations of metal-organic interfaces, the similarity between the work functions of PEDT/PSS and Au provides an excellent opportunity to examine basic issues related to the formation of interfaces on otherwise fundamentally different substrates. The electronic structure of most metal-organic molecular semiconductor interfaces investigated so far departs from the simple Schottky-Mott limit and exhibits a substantial (~ 0.5 – 1.0 eV) interface dipole barrier.^{2,3} Recent experimental and theoretical studies have suggested that a significant fraction of the interface dipole barrier at organic-on-metal interfaces corresponds to a lowering of the metal ϕ by the adsorbed molecules.^{4,5} Indeed, the work function of a metal is comprised of both bulk and surface-dipole

contributions,⁵⁻⁶ the latter corresponding to the tail of electrons spilling out from the metal surface into the vacuum. This surface-dipole contribution is always substantially modified by the presence of an adsorbate. In the case of large adsorbates, such as conjugated organic molecules, the repulsion between the molecule electrons and the metal surface electrons leads to a compression of the electron tail leading to a lowering of the metal work function. This, in turn, causes an abrupt downward “shift of the vacuum level” from the metal to the organic film at the interface, i.e., a surface dipole barrier. The consequence of this systematic lowering of the metal ϕ is a downward shift of the molecular energy levels and an increase in the energy difference between the metal Fermi level (E_F) and the highest occupied molecular orbital (HOMO) of the organic film. The hole injection barrier is, therefore, systematically increased with respect to a vacuum level alignment situation, with the unfortunate consequence of a significant reduction in current injection performance. The reduction in metal work function being difficult to assess, a reliable prediction of the injection barrier is also difficult. On the other hand, a conducting organic polymer like PEDT/PSS is made of closed-shell molecules and has much fewer free electrons than a metal like Au. Its work function does not have a significant surface electron tail contribution, and should not undergo the type of modification just described. This, in turns, should enable the formation of smaller hole injection barriers at a contact with a conjugated organic material (COM), as compared to a contact with a high work function metal.

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In the present study, we (i) report hole injection barriers measured directly with ultraviolet photoemission spectroscopy (UPS) at interfaces between three organic molecular materials and two high work function electrode materials (Au and PEDT/PSS) and (ii) demonstrate the conceptual differences between the mechanisms leading to energy level alignment for a metal and a polymer electrode. The three organic materials are *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1-biphenyl-4,4'-diamine (α -NPD), used as a hole transport layer in organic light-emitting devices,⁷ pentacene, used as active material in field-effect thin-film transistors,⁸ and *para*-sexiphenyl (6P), which can be employed in both types of devices.^{9,10}

Sample preparation and UPS measurements were made in ultrahigh vacuum (UHV) systems comprising interconnected preparation and analysis chambers at Princeton University, or on beamline E1¹¹ (FLIPPER II) at HASYLAB, Hamburg (Germany). The base pressure in both systems was below 5×10^{-10} mbar. The metal substrates consisted of *in situ* sputtered thin films of polycrystalline gold deposited on silicon wafers precoated with a thin layer of chromium, or on mica. Thin films of PEDT/PSS (Baytron[®] AI4083) were spin coated *ex situ* onto cleaned ITO covered glass slides and annealed in ambient atmosphere at 150 °C. They were subsequently transferred into the UHV system. The organic materials were evaporated in steps in the preparation chambers from resistively heated pinhole sources, at a pressure lower than 4×10^{-9} mbar. The thickness of each film was monitored with a quartz microbalance placed next to the substrates. No corrections for possible differences in sticking coefficient between the microbalance and the actual sample were made. The work function of the samples was determined by applying a negative bias to the sample to clear the detector work function and recording the secondary electron cutoff.¹² The ionization energy (IE) of the COMs was also determined using the cutoff.¹² In the present experiments, the photon energy for recording the photoemission spectra was 21.2 eV (HeI resonance line) for the system in Princeton, and 22 eV at HASYLAB. The resolution of the UPS measurements was 0.15 eV in both cases.

The work function of the substrates was determined first. For different PEDT/PSS films, the values for ϕ ranged from 4.80 to 5.15 eV. We attribute the variations to changes in the surface composition of the films due to slight differences in preparation conditions and time lapsed between spin coating and introduction into the UHV chamber. However, the UPS valence spectra of the films with different ϕ were virtually identical. The freshly sputtered Au films that served as substrates for α -NPD and 6P deposition had a ϕ of 5.1 eV. For the deposition of pentacene, an Au film grown on mica was sputtered *in situ*, resulting in a work function of 5.4 eV; this higher value of ϕ is due to the predominant (111) orientation of the Au islands on mica.¹³

The organic materials were evaporated in steps onto the substrates, from submonolayer coverage (typically 2 Å) to a thickness for which no signal from the substrate could be detected (except for pentacene/Au). Photoemission spectra were measured after every deposition. For the three COMs deposited on PEDT/PSS, the energy difference between the organic molecular levels and the substrate Fermi level (E_F)

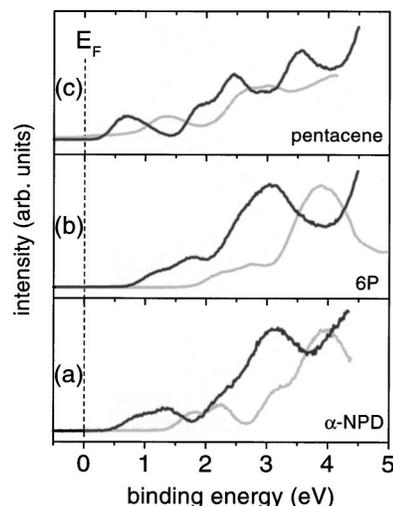


FIG. 1. UPS spectra of COMs deposited on Au (gray curves) and PEDT/PSS (black curves). The photon energy is 22 eV, unless otherwise noted. (a) α -NPD; 100 Å on Au and 40 Å on PEDT/PSS. (b) *p*-sexiphenyl; 200 Å on Au and 64 Å on PEDT/PSS. (c) pentacene; 150 Å on Au ($h\nu=21.2$ eV), and 64 Å on PEDT/PSS. The zero of the binding energy scale corresponds to the Fermi level.

was constant (within ± 0.1 eV at different sample spots) throughout the deposition sequence. On Au, on the other hand, the molecular levels exhibited a rigid shift of ~ 0.2 eV (± 0.1 eV) toward higher binding energy (with respect to E_F) from submonolayer/monolayer coverage to several monolayers. No further shift of the organic levels was observed after this initial one. This shift is attributed to a change in polarization due to a decrease in the screening of the photohole by metal electrons, as the distance between the photoexcited molecule and the metal substrate increases with film thickness.¹⁴ No similar change in polarization is observed for the polymer substrate, which does not possess the density of free electrons available in the metal.

The valence electron spectra of the three COMs deposited on the two different substrates are shown in Fig. 1. As noted earlier, for pentacene on Au [gray curve in Fig. 1(c); nominal pentacene thickness: 150 Å] a small photoemission intensity from the Au substrate (at and near E_F) is still visible. This is due to the fact that pentacene grows in a Stransky–Krastanov-type mode on Au,¹⁵ resulting in pronounced island growth for multilayers (observed *ex situ* by atomic force microscopy). Given that the molecular levels in these films are flat away from the interface (as mentioned herein), one can measure from these spectra the injection barriers for holes (ϕ_h) from the substrate into the organic material. The barrier is equal to the energy difference between E_F and the low binding energy onset of the HOMO. The key result here is that all the ϕ_h measured for PEDT/PSS are significantly lower than for Au, in spite of a very similar initial electrode ϕ : 0.4 eV versus 1.4 eV for α -NPD, 0.75 eV versus 1.8 eV for 6P, and 0.25 eV versus 0.85 eV for pentacene. A schematic energy level diagram of the interfaces is shown in Fig. 2. [The position of the lowest unoccupied molecular orbital (LUMO) of α -NPD and pentacene are obtained from inverse photoemission experiments.]^{16,17} In one additional UPS experiment (data not shown here), 6P was deposited onto a PEDT/PSS film with an initial ϕ of 5.05 eV. ϕ_h was found to be identical within 0.1 eV to the

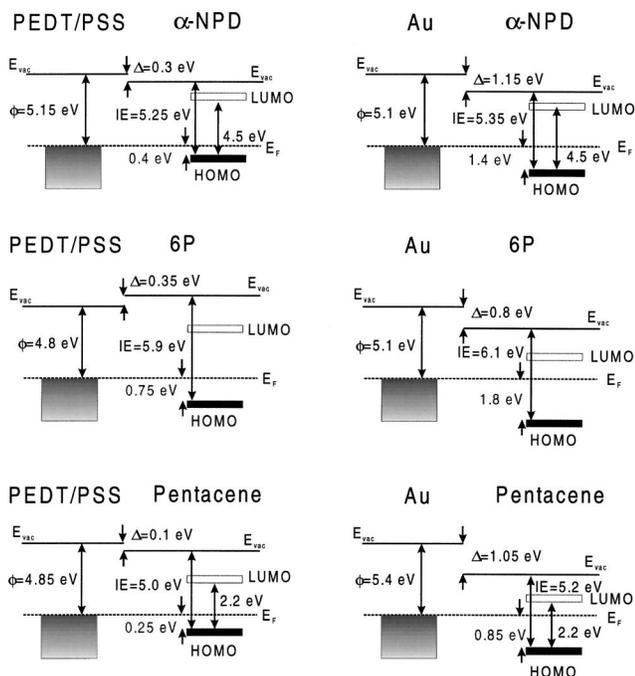


FIG. 2. Schematic energy level diagrams of the interfaces between the three COMs and Au and PEDT/PSS, showing the Fermi level E_F , HOMO and LUMO, the vacuum levels (E_{vac}) and IE, and the interface dipole Δ . The positions of the HOMO and LUMO are derived from photoemission measurements. The position of the LUMO of α -NPD and pentacene are obtained from inverse photoemission experiments.

one obtained for an initial substrate ϕ of 4.80 eV. Figure 2 also displays the values of the interface-dipole Δ (i.e., the vacuum level offset) obtained from the shift of the secondary electron cutoff, and the ionization energy of each COM. The Δ 's are consistently much larger for Au (1.15 eV for α -NPD, 0.8 eV for 6P, and 1.05 eV for pentacene) than for PEDT/PSS (0.3 eV for α -NPD, -0.35 eV for 6P, and 0.1 eV for pentacene). The minus sign for 6P on PEDT/PSS indicates a dipole barrier of *opposite* sign, i.e., the vacuum level rises from the polymer electrode to the molecular film.

It should be emphasized that no evidence of chemical reaction or formation of interface electronic states in the gap of the organic film is obtained from UPS for any of the six interfaces investigated. The similarity of observations made for three very different molecular compounds leads, therefore, to an important general result. The explanation for the large interface dipole observed at the COM/Au interfaces is the change of the metal surface dipole contribution to the work function upon adsorption of the molecules. The electron density tailing from the free surface into vacuum is pushed back into the solid upon adsorption, thus reducing the surface dipole and effectively decreasing the work function of the covered surface.⁴ This leads to the relatively large interface dipole and ϕ_h values, in spite of the large initial electrode ϕ . In contrast, the work function of PEDT/PSS is mainly controlled by the energy levels created by the charge transfer between the sulfonate and the ethylenedioxythiophene moieties.¹⁸ This charge transfer does lead to dipoles within the polymer, but they have random orientation and cancel each other macroscopically. The surface electron dipole layer contribution to the work function is minimal,

and the adsorption of molecules modifies only slightly the work function of the polymer. The resulting interface dipole barriers Δ and the hole injection barriers ϕ_h are, therefore, systematically smaller (by ~ 0.6 – 1 eV) than those measured for the metallic electrode. We note that the magnitude of the Δ found at the COM—PEDT/PSS interfaces is compatible with those generally obtained at organic—organic interfaces.¹⁹ It is determined by the precise nature of chemical interactions and charge transfer between the COM and PEDT/PSS, which are still to be determined. Current investigations are being directed toward this issue.

In summary, we have shown by photoemission spectroscopy that the hole injection barrier at interfaces between three conjugated organic materials (α -NPD, 6P, and pentacene) deposited on PEDT/PSS is drastically smaller than on Au, although the two substrates have a similar work function (~ 5 eV). The difference is linked to one of the basic mechanisms of molecular level alignment on metal surfaces, i.e., the reduction by adsorbed molecules of the surface electronic tail contribution to the work function of a metal. Upon adsorption, the metal ϕ is lowered, leading to a large hole injection barrier. The smaller surface electronic contribution to the work function on a material like PEDT/PSS leads to the much more favorable energy level alignment for hole injection.

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