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Electrical doping: the impact on interfaces of π -conjugated molecular films

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Abstract

Organic–metal and organic–organic interfaces play crucial roles in charge injection in, and transport through, organic thin film devices. Their electronic structure, chemical properties and electrical behaviour must be fully characterized and understood if engineering and control of organic devices are to reach the levels attained for inorganic semiconductor devices. Recent fundamental, as well as device, work has demonstrated that electrical doping provides a very interesting way to improve carrier injection into molecular films and, eventually, control molecular level alignment at their interfaces. This brief review emphasizes the current understanding of the effects of doping on organic interfaces.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The development of organic materials and devices with application in light emission, light–energy conversion and thin film electronics has received considerable attention over the past few years. A characteristic common to all these devices is their being based on thin film architectures, which place special emphasis and demands on charge carrier injection and transport through interfaces. These devices often comprise multiple layers of organic materials and contacts for electron or hole injection, making metal–organic (MO) and organic–organic (OO) interfaces exceedingly important in terms of device performance. These interfaces can at times appear to be difficult hurdles to overcome, or instead present real opportunities for improving device performance. For example, the large injection barriers often found between metals and large gap organic materials are serious impediments to charge injection, and can cause a variety of problems ranging from high turn-on voltages to device degradation. On the positive side, the advanced architecture of organic light

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emitting diodes (OLED) and photovoltaic cells has been shown to make successful use of multiple organic layers with different energy gaps in engineering molecular level offsets across OO heterojunctions and blocking unwanted carrier transport or recombination of excitons, thus enhancing quantum efficiency. Given their obvious importance, these MO and OO semiconductor interfaces have been the subject of multiple fundamental and phenomenological investigations aimed at understanding their electronic and chemical structure, and at controlling interface energy barriers [1–3].

This short review looks at electrical doping as a means of modifying/controlling interfaces. Electrical doping of organic molecular films has been investigated relatively little as compared to doping of inorganic semiconductors at the same stage of development of these materials. The main reason is that, unlike in inorganic semiconductors, traditional n and p doping has not been a requirement for achieving bipolar transport in the most common molecular device, i.e. the OLED. The ability to move away from the basic pn homojunction by stacking or combining *electron transport* and *hole transport* organic layers alleviates the need to ‘dope’ the materials to inject electrons and holes into the active layer(s). However, the performance of organic devices is now reaching levels at which electrical doping looks attractive as a means of further improving efficiency by enhancing carrier injection and lowering drive voltages. In the past few years, electrical doping of molecular films by insertion of electron donating (n dopants) or electron accepting (p dopants) atoms or molecules has been shown to be efficient and to increase film conductivity by several orders of magnitude. The p-type doping of hole transport materials (HTM) using antimony pentachloride (SbCl_5) [4] and iron trichloride (FeCl_3) [5] has been investigated. So far, however, the most widely investigated p dopants for organic films are tetracyanoquinodimethane (TCNQ) and its fluorinated derivative tetrafluorotetracyanoquinodimethane ($\text{F}_4\text{-TCNQ}$), a strong organic electron acceptor [6–11]. The n-type doping of electron transport materials with alkali metal atoms [12–16] has been extensively investigated, but these metals may not be suitable for controlled doping. Electron donating organic molecules are also beginning to be investigated [17].

Several basic preliminary remarks should be made about doping in molecular materials. First, the organic matrix is, in essence, far less strongly coordinated than the inorganic matrix. Molecules are bound by weak van der Waals (vdW) forces, instead of strong interatomic covalent bonds. Doping occurs by direct charge transfer of electrons from host to dopant for p type and in the opposite direction for n type, rather than by incorporation of the dopant via formation of covalent bonds and release of excess charge (electron or hole) to a band, as occurs in inorganic semiconductors. Second, the physics of charge transport in molecular films is dominated by localization and polarization [18]. The intermolecular overlap of wavefunctions is small and transport is by thermally activated hopping. The charge released by the dopant to the host molecule is far less delocalized than in inorganic semiconductors, and charge–dopant separation does not occur as readily. Third, by virtue of the vdW bonds, the organic matrix is much softer and can withstand more distortion than the inorganic matrix upon insertion of dopant atoms or molecules (up to a few per cent). Furthermore, because of increased localization, dopant–dopant interaction is weaker and doping concentrations can be pushed significantly higher than in inorganic semiconductors without leading to spurious effects, such as ‘banding’.

Electrical doping of molecular layers has been shown to be extremely useful in organic-based devices. As an example, Yamamori *et al* [19] demonstrated that p doping of a hole transport poly-carbonate polymer with tris(4-bromophenyl)aminium hexachloroantimonate (TBAHA) allowed one to extend the thickness of the polymer layer to 500 nm while keeping the drive voltage low (5–6 V) and increasing the electroluminescence efficiency of the OLED. In another example, Zhou *et al* [20] used a 100 nm

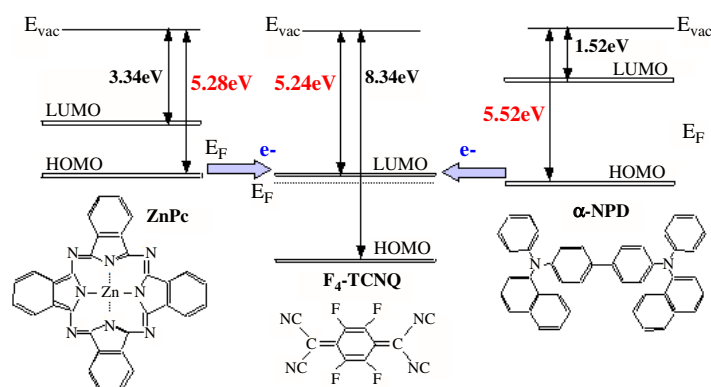


Figure 1. Electronic structure, i.e. the IE and EA, of ZnPc, α -NPD and F₄-TCNQ determined by a combination of UPS and IPES. The chemical structure of the molecules is represented.

4,4',4''-tris(3-methylphenylphenylamino)-triphenylamine (m-MTDATA) hole transport layer p doped with F₄-TCNQ in a three-organic-layer OLED and demonstrated a record-breaking drive voltage and high efficiency. As organic devices are slowly moving toward commercialization, there is therefore a considerable incentive to achieve a better understanding of doping mechanisms and the opportunities that doping offers in terms of device improvement.

This paper reviews work on doping from the point of view of MO and OO interfaces and their energetics. It describes the extent to which MO and OO energy barriers are changed by doping the molecular film, and reports on the consequences of these modifications in terms of charge injection. This introduction is followed by a brief description of our experimental approach. The results on doping are organized in three sections. The first describes the electronic structure of the host and dopants, demonstrates doping in two HTMs and looks at the effect of doping on the position of the Fermi level in these materials. The second gives results concerning MO interface energetics and the depletion region, and demonstrates that charge carrier tunnelling through the depletion region is responsible for the remarkable increase in current injection in the doped layers. The third and final section describes very recent results on doping-induced changes in molecular level offsets at OO interfaces.

2. Experimental approach

All the experiments are performed in ultrahigh vacuum (UHV) in a triple-chamber vacuum system, for surface analysis, organic growth and electrical characterization. The overall methodology consists of depositing incrementally an organic film, and using ultraviolet photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPES) and the contact potential difference (CPD) with a Kelvin probe (KP) to measure interface energy barriers and molecular level shift ('band bending') away from the interface. Current–voltage (I – V) measurements are also carried out *in situ* on complete diodes, the structure of which is specified below.

The films investigated here are made of small molecules evaporated from solid sources. The molecules are zinc phthalocyanine (ZnPc) and N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD), two HTMs with application in organic devices. These organic materials, which are commercially available, are purified *ex situ* by gradient sublimation and placed in simple crucibles in the UHV growth chamber. The dopant used

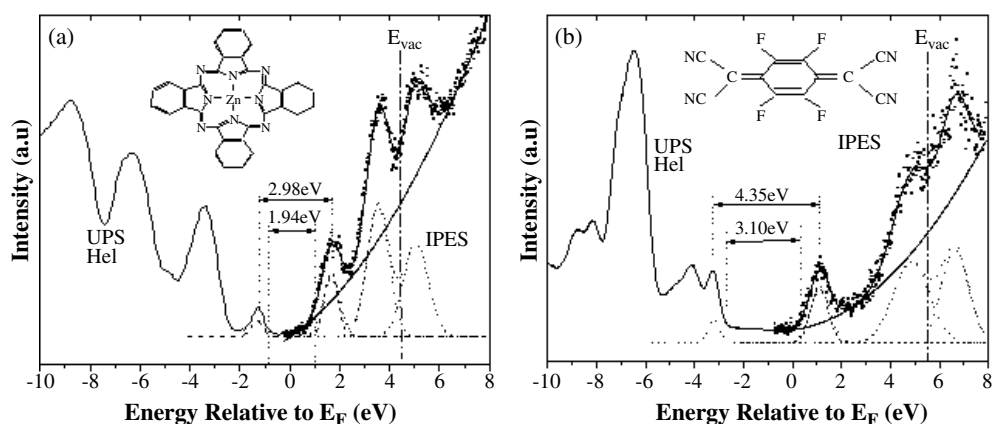


Figure 2. Combined UPS-IPES spectra of a 100 Å thick film of (a) ZnPc and (b) F₄-TCNQ.

in the work reviewed here is F₄-TCNQ. The chemical structure of the three molecules is given in figure 1. Doped films are made by co-evaporation, with host and dopant fluxes controlled independently to achieve the desired doping level. The dopant concentration is evaluated via x-ray photoemission spectroscopy. Typical dopant (molecular) concentrations range up to ~0.5–3%, although larger concentrations (up to 5% and higher) can be achieved by cooling the substrate upon film deposition. UPS is used to measure the photoemission cut-off, which gives the position of the vacuum level (E_{vac}) of the film, and the position of the valence states and highest occupied molecular orbital (HOMO) as a function of doping and film thickness. IPES is used to measure empty states and compare the energy position of the p-dopant (F₄-TCNQ) lowest unoccupied molecular orbital (LUMO) to that of the host HOMO. The resolutions of the UPS and IPES measurements are 0.15 and 0.45 eV, respectively. Finally, CPD measurements are performed to verify that the shifts of E_{vac} and the molecular levels are independent of photon irradiation, and to detect eventual photoemission-induced effects such as photovoltage. The combination of these techniques plus $I-V$ measurements performed *in situ* provides a detailed picture of the energetics of doped MO and OO interfaces and of their impact on charge carrier injection.

3. Electronic structure of host, dopant and doped films

The combined UPS and IPES spectra from 100 Å thick pure ZnPc and F₄-TCNQ films deposited on metal substrates are shown in figure 2 [10]. HOMO and LUMO peaks at -1.2 and +1.8 eV for ZnPc and -3.2 and +1.1 eV for F₄-TCNQ, respectively, are well resolved, allowing a precise determination of the ionization energy (IE) and electron affinity (EA) of each compound. In our work, the IE and EA of the condensed organic film are conventionally defined as the energy differences between E_{vac} , obtained from the photoemission onset, and the leading edges of the HOMO and LUMO peaks, respectively. The energy scales of the UPS and IPES spectra are aligned by matching the Fermi energies obtained with the two techniques from the metallic substrate (Au in the present case). Similar UPS/IPES measurements were performed on films of α -NPD [21], the other HTM of interest here.

The electronic structures obtained from UPS and IPES measurements on pure ZnPc, α -NPD and F₄-TCNQ films are summarized in figure 1. The IEs of ZnPc and α -NPD are 5.28 and 5.52 eV, respectively, and the EA of F₄-TCNQ is 5.24 eV. The IE and EA of F₄-TCNQ

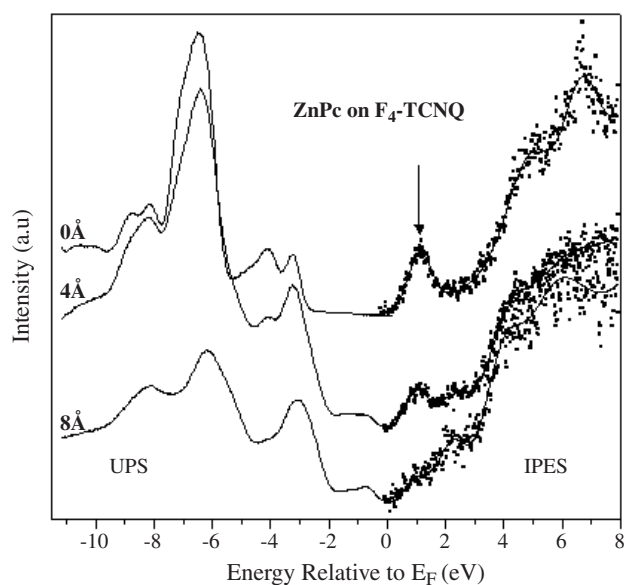


Figure 3. Combined UPS–IPES spectra of an F_4 -TCNQ film as functions of incremental deposition of ZnPc. The arrow marks the IPES feature corresponding to the F_4 -TCNQ LUMO, which is rapidly attenuated upon filling by ZnPc electrons.

are among the highest reported for π -conjugated molecular films [22, 23], suggesting that the molecule is adequate as an efficient electron acceptor in a number of molecular compounds.

The excellent match between the IEs of ZnPc and α -NPD and the EA of F_4 -TCNQ suggests an energetically favourable electron transfer from the HOMO of either of these two hosts and the LUMO of the dopant, resulting in effective p-type doping. One should note, however, that the EA of F_4 -TCNQ is measured for molecules in a pure F_4 -TCNQ film, i.e. a molecular environment that is different from that encountered by F_4 -TCNQ molecules dispersed in ZnPc or α -NPD. The direct comparison of the EA of the guest and IE of the host, made above to assess doping efficiency, makes the implicit assumption that the polarizations experienced by the negatively charged F_4 -TCNQ molecular ion created by IPES [24] are the same in the two environments. This assumption is generally valid to within a few tenths of an electronvolt for a number of molecular compounds [22].

The host-to-dopant charge exchange is unambiguously demonstrated by the following experiment [10]. A thin film (a few nanometres) of dopant molecules is deposited on a metallic surface (kept at 250 K to increase the sticking coefficient) and incrementally covered with an overlayer of ZnPc. The UPS and IPES spectra recorded as a function of ZnPc thickness are shown in figure 3. The pristine F_4 -TCNQ film displays a strong LUMO peak (the arrow at 1.1 eV above E_F). This feature is rapidly attenuated upon deposition of ZnPc, indicative of the charge transfer and filling of the F_4 -TCNQ LUMO with electrons from the HOMO of the overlayer molecules. The higher F_4 -TCNQ empty states are less affected, except for the growth of the ZnPc LUMO peak at ~ 2.5 eV. On the side of filled states, the F_4 -TCNQ HOMO at -3.2 eV is masked by the intense ZnPc HOMO-1 peak, while the former F_4 -TCNQ gap is progressively filled by the ZnPc HOMO (~ -0.7 eV).

We now look at the effect of doping on the position of the Fermi level (E_F) in the material. A homogeneously doped 100 Å film of ZnPc or α -NPD is deposited on Au and the HOMO

Table 1. The position of the Fermi level at room temperature above the leading edge of the HOMO in ZnPc and α -NPD deposited on Au (with a work function of ~ 5.1 – 5.2 eV), as a function of F₄-TCNQ concentration.

F ₄ -TCNQ (%)	0 (eV)	0.3–0.5 (eV)	3 (eV)	5 (eV)
ZnPc	0.9	0.42	0.18	—
α -NPD	1.24	0.62	—	0.36

level is measured with respect to E_F . It is important to specify the nature of the substrate, as the position of E_F in the bulk of the undoped organic film is defined primarily at the interface by the metal work function and the organic/metal interaction [25–28]. The positions of E_F in intrinsic and doped ZnPc and α -NPD deposited on Au are summarized in table 1 [9, 10, 21]. Note that E_F approaches to within 0.36 eV of the α -NPD HOMO edge when the doping level is increased to several per cent, but never reaches the 0.18 eV obtained in ZnPc. Two reasons are possible here. First, the energy difference between the host HOMO and F₄-TCNQ LUMO is larger in α -NPD (0.28 eV) than in ZnPc (0.04 eV), although the charge transfer ratios between host and dopant molecules were found via FTIR to be nearly the same: 0.6 for α -NPD:F₄-TCNQ versus 1 for ZnPc:F₄-TCNQ [7]. Second, and more fundamental, is the difference between the relaxation energies of α -NPD and ZnPc. As the host molecule is ionized and occupied by a hole, its charge-induced relaxation pushes the partially empty HOMO upward into the organic gap. Larger non-planar molecules such as TPD and biphenyl undergo substantial geometrical relaxation upon ionization. The relaxation energy is of the order of 0.15–0.19 eV [29] for these molecules versus less than 0.05 eV for ZnPc [30]. α -NPD has a molecular structure very similar to that of TPD, with its HOMO localized on the two benzene rings of the central biphenyl core and the lone pairs of the two adjacent nitrogen atoms [31]. Similar molecular relaxation energy is expected in these two materials. We suggest therefore that this relaxation energy contributes to pushing the partially occupied HOMO of the ionized α -NPD molecule further up in the gap than in the case of ZnPc. This state pins the Fermi level and leads to a larger energy difference between E_F and the HOMO in α -NPD:F₄-TCNQ than in ZnPc:F₄-TCNQ [21].

The next, and perhaps more important, question is whether the hole induced in the host molecule by this charge transfer is mobile or localized near the dopant counter-ion. We see next that the formation of a depletion region at the metal/doped organic layer interface provides an answer to this question.

4. Energetics of interfaces: undoped versus doped organic film on Au

The UPS spectra of undoped α -NPD deposited on Au, including the onset of photoemission, are shown in figure 4(a) as a function of thickness. The bottom spectrum corresponds to clean Au. The deposition of a fraction of a molecular layer of α -NPD (~ 4 Å) causes the (now well documented) shift of the onset of photoemission toward higher binding energy [2, 28], which is equivalent to a downward shift of E_{vac} for the metal. The shift is complete with the first molecular layer (16 Å), and totals nearly an electron volt. It signals the formation of an interface dipole barrier linked to the modification of the metal work function by adsorption of the molecules [26, 32–34]. Beyond the first molecular plane, the vacuum level remains flat with increasing film thickness, at least on a thickness scale compatible with thin film devices (several 100 Å) and consistent with the intrinsic nature of undoped α -NPD. E_F is near mid-gap at 1.24 eV above the leading edge of the HOMO. The figure also shows that the HOMO level measured by UPS shifts by 0.2 eV to higher binding energy when the coverage increases from 4 to 32 Å [21].

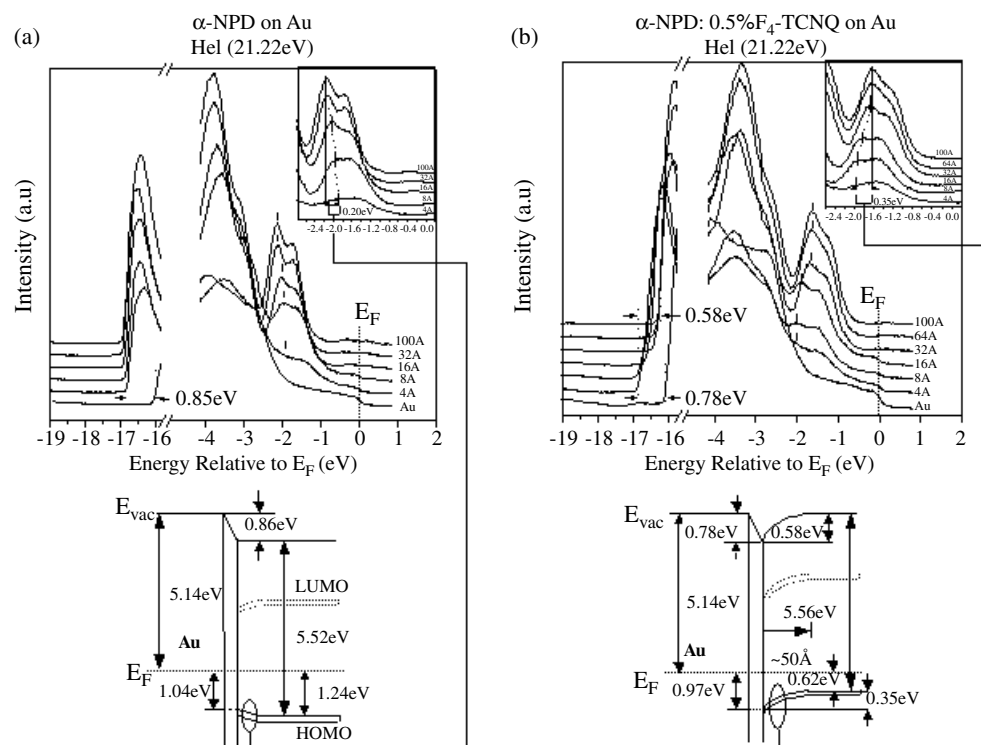


Figure 4. UPS spectra (top) and a schematic diagram of the interface electronic structure (bottom) for α -NPD films incrementally deposited on Au: (a) undoped α -NPD; (b) α -NPD:0.5% F₄-TCNQ. The binding energies are referenced to E_F measured on Au. The insets show the shift in the α -NPD HOMO with background signals from the Au substrate removed for clarity.

This shift does not represent a ‘molecular level bending’, and is attributed to the decrease in polarization energy of the photoemission-generated hole from the organic–metal interface, where polarization due to the metal is the largest, to the surface of the thick film [35, 36]. The measured increase in E_{vac} -HOMO signals a polarization-related increase in IE for the molecule from interface to film surface. Similarly, the LUMO level is expected to undergo a shift of comparable magnitude in the opposite direction due to a polarization-induced decrease in the EA of the molecule from interface to surface. Such a shift has been measured by IPES and scanning tunnelling spectroscopy on PTCDA molecules [36], but these measurements have not yet been extended to α -NPD. The LUMO level shift is therefore plotted as a dotted line here.

The UPS spectra and onset of photoemission as a function of deposition of uniformly doped α -NPD (0.5%F₄-TCNQ) are shown in figure 4(b). The interface dipole is reduced by 0.08 eV with respect to the undoped case. E_{vac} , the HOMO and all valence levels (once corrected for the polarization shift explained above) gradually shift upward with increasing layer thickness, indicative of the formation of a space charge region with upward molecular level bending. The complete bending of 0.58 eV is reached at ~ 64 Å. Considering the uncertainties in layer thickness and dopant incorporation, this is in good agreement with the estimate of 50 Å obtained from a standard electrostatic calculation using a doping concentration of 0.5%, a dielectric constant $\epsilon = 3$ and a unity charge transfer. Evidence of a space charge region is also obtained for doped ZnPc layers grown on Au [9, 10]. In that case, the thickness of the space charge region is ~ 130 Å for 0.3% doping and ~ 30 Å for 3% doping (figure 5).

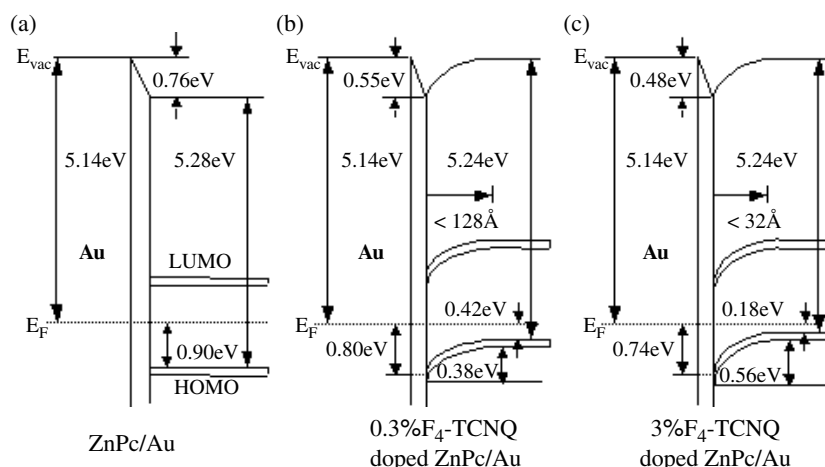


Figure 5. The energy of the molecular levels near the interface between Au and (a) undoped ZnPC; (b) ZnPC:0.3% F₄-TCNQ; (c) ZnPC:3% F₄-TCNQ. The measured width of the depletion region is shown in (b) and (c). The interface dipole, the work function of Au and the ZnPC IE are indicated in each case.

Photoemission spectroscopy, UPS in particular, can in certain cases induce surface photovoltage (SPV), which affects the measurement of the molecular level position, e.g. E_F –HOMO. In SPV, electron–hole pairs generated by the radiation near the surface or, in the present case, the interface are separated by the built-in electric field of the space charge region. If the minority carriers accumulate at the interface, they create a field that opposes the built-in electric field of the space charge region and lead to an erroneous E_F -to-valence band energy distance [37, 38]. SPV is typically stronger in low doped and large gap semiconductors, and thus could affect the UPS measurements on the molecular films considered here. This possibility is investigated using CPD measurements with a KP. The CPD measurements are done in the dark and cannot induce SPV. Figure 6 shows that UPS and KP measurements yield identical changes in work function (within experimental errors) versus α -NPD thickness for undoped as well as for 0.5% doped films. The two sets of curves display the same initial drop in work function (or E_{vac}) associated with the formation of the interface dipole. The subsequent increase corresponds to the upward molecular level bending in the interface depletion region. The excellent agreement between CPD and UPS data on both undoped and doped films demonstrates therefore that SPV does not play a significant role in the UPS measurements reported above.

An important observation is that the interface energy barriers of the doped films are nearly identical to those of the undoped films: 1.04 and 0.9 eV for undoped α -NPD and ZnPC, respectively, versus 0.97 and 0.8 eV for their 0.5 and 0.3% doped counterparts. This indicates that the anchoring of the molecular level at the metal/organic interfaces is strong enough to resist doping and the shift of the Fermi level in the bulk of the material. The energy level alignment at the MO interface depends on a variety of mechanisms, which are beyond the scope of this paper but have been reviewed in detail elsewhere [26–28, 39]. Yet, in spite of the fact that the barrier is nearly independent of the doping, the hole injection current is 5–7 orders of magnitude larger for the doped films than for the undoped films. Figure 7 displays the hole current as a function of voltage applied across three Au/ α -NPD/Au devices with the same basic structure (see the inset): the first (●) includes of a 1700 Å thick layer of undoped α -NPD; the second (*) includes 80 Å of α -NPD:0.5% F₄-TCNQ near the bottom Au contact

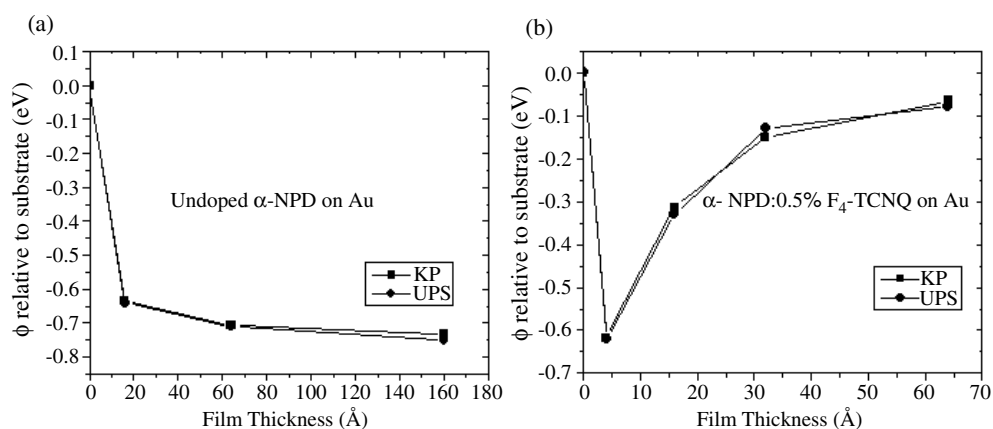


Figure 6. Comparison of changes in work function measured with a KP and UPS for (a) undoped α -NPD and (b) α -NPD:0.5% F_4 -TCNQ incrementally deposited on Au.

and 1620 Å undoped α -NPD; and the third (○) includes a 1700 Å layer of homogeneously doped α -NPD:0.5% F_4 -TCNQ. In these I - V measurements, the polarity corresponds to holes injected from the *bottom* electrode. The current in the second device is almost four orders of magnitude larger than that of the first at 6 V, clearly due to doping-induced enhancement of the hole injection since 95% of the organic film is undoped. Therefore, the current in the first device is injection limited, and the current enhancement in the second device is due to hole tunnelling through the narrow depletion region shown in figure 4(b). The further enhancement in the third device indicates that hole transport in the second device is limited by the bulk and is trap charge limited. The total hole current enhancement due to doping is therefore between four and seven orders of magnitude, and due to tunnelling through the depletion region. Similar current enhancement via hole tunnelling is obtained at the interface between the Au and doped ZnPc [10], indicating a general phenomenon related to the formation of a narrow depletion region at a MO interface. One can thus reasonably expect doping to play a major role in future designs of high efficiency, low turn-on voltage devices.

5. Doping impact on organic–organic heterojunctions: formation of an interface dipole

Understanding and controlling the electronic structure of OO heterojunctions is very important as well, since molecular level alignment between different organic materials controls the transport of electrons and holes across multilayer devices. We start here from a slightly different point: unlike at MO interfaces, where the vacuum level alignment rule generally breaks down, vacuum level alignment is observed at the majority of interfaces between undoped organic materials [28, 40]. Examples are given in figures 8(a) and (c). The electronic structure of these heterojunctions is derived from UPS measurements on bathocuproine (BCP) and 4,4'- N,N' -dicarbazolyl-biphenyl (CBP), two electron transport materials (ETM), incrementally deposited on undoped α -NPD and ZnPc. Vacuum level alignment is observed at both interfaces. The HOMO offset across the interface, which is the hole barrier, is the difference between the IEs of the two organics. Similarly, the offset between the LUMOs, or electron barrier, is the difference between the electron affinities.

The impact of doping on the electronic structure of OO interfaces is rather different than that for MO interfaces. Instead of fixed HOMO and LUMO offsets and formation of

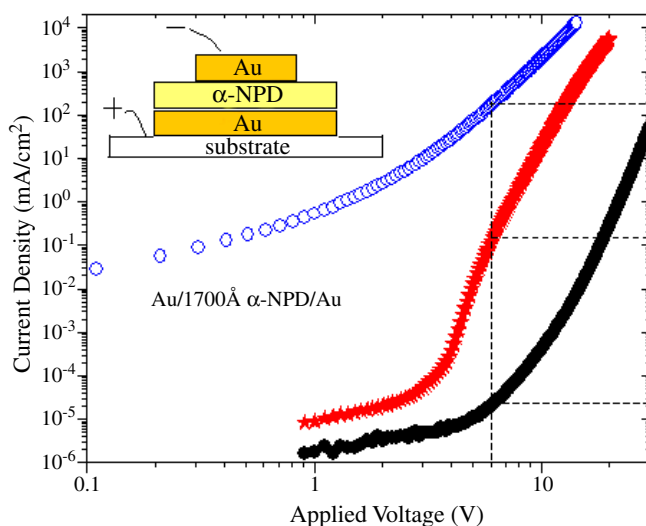


Figure 7. I - V characteristics of three different Au/ α -NPD/Au devices: (●) 1700 Å of undoped α -NPD (a type I device); (*) 80 Å of α -NPD:0.5% F₄-TCNQ + 1620 Å undoped α -NPD (a type II device); (○) 1700 Å of α -NPD:0.5% F₄-TCNQ (a type III device).

a space charge region to compensate for the doping-induced movement of E_F in one of the two materials, we observe the formation of a significant interface dipole Δ accompanied by a corresponding shift in molecular level offsets. Δ compensates for the doping-induced E_F movement in the doped layer, while molecular levels remain flat away from the interface in each material (figures 8(b) and (d)) [41]. In the case of BCP deposited on α -NPD:0.5% F₄-TCNQ, the vacuum level shifts by 0.6 eV and the HOMO offset correspondingly increases to 1.64 eV (figure 8(b)). The α -NPD HOMO energy remains unchanged during the deposition of BCP.

A very similar situation is observed for CBP on doped ZnPc. The vacuum level shift is 0.5 eV and leads to a corresponding change in the ZnPc/CBP molecular level alignment. At these heterojunctions, the movement of the HOMO of the top ETM follows the downward movement of E_F in the HTL (figures 8(b) and (d)), in the opposite direction to what would be expected if p cross-doping of the ETL by F₄-TCNQ was an issue. Cross-doping can therefore be eliminated from consideration as the cause of the interface dipole.

The results from these two HTL/ETL heterojunctions demonstrate that molecular level offsets at OO interfaces can be changed by adjusting the Fermi level position in the HTL via doping. To test whether Fermi level shift or doping is the enabling step, we perform an experiment where E_F is moved by changing the work function of the substrate without doping the HTL layer. E_F moves linearly, although not necessarily with a slope equal to one, in the energy gap of a number of organic materials as a function of the work function of the metal substrate [2, 28, 39]. As an example, the deposition of undoped α -NPD on Mg (with a work function of 3.65 eV) leads to a position of E_F nearly 1 eV higher with respect to the HOMO than that obtained for deposition on Au (with a work function of 5.14 eV) [3, 39]. This shift, however, does not induce a dipole or change the HOMO and LUMO offsets at the interface (figure 9), in contrast with the case for the doped interface.

The validity of the Fermi level as a meaningful equilibrium level through a 100–150 Å film of wide gap (nearly insulating) materials must be evaluated. To do this, we grew two structures



Figure 8. The electronic structure of the (a) undoped α -NPD/BCP interface; (b) α -NPD:0.5% F_4 -TCNQ/BCP interface; (c) undoped ZnPc/CBP interface; and (d) ZnPc:3% F_4 -TCNQ/CBP interface. All heterojunctions are grown on Au (with a work function of 5.14 eV).

with the doped layer on top: CBP(100 Å)/ α -NPD:0.5% F_4 -TCNQ on Au and on Mg. The UPS measurements (including data analysis to extract the CBP valence states masked by the α -NPD states) show that the CBP energy levels shift upward upon deposition of the doped α -NPD layer. The key point is that the α -NPD HOMO follows the Fermi level movement caused by the replacement of Au by Mg, so as to keep the 0.62 eV value of E_F -HOMO imposed by doping (figure 10). This demonstrates unambiguously that E_F remains a meaningful equilibrium quantity across these relatively thin films.

The main conclusion is therefore that doping-induced E_F movement, rather than substrate-induced E_F movement, leads to the formation of the interface dipole and modification of the molecular level alignment at OO interfaces. Preliminary results on other interfaces suggest that this is a general phenomenon. The movement of E_F through the OO heterojunction caused by the remote change in substrate work function has little impact in terms of modulating interface charges in these wide gap materials. HOMO and LUMO offsets remains defined by vacuum level alignment. On the other hand, E_F movement due to doping is directly linked to the introduction of charges at or near the OO interface (holes, in the present case). It is likely that these carriers play an important role, such as occupation of states on one side or the other of the

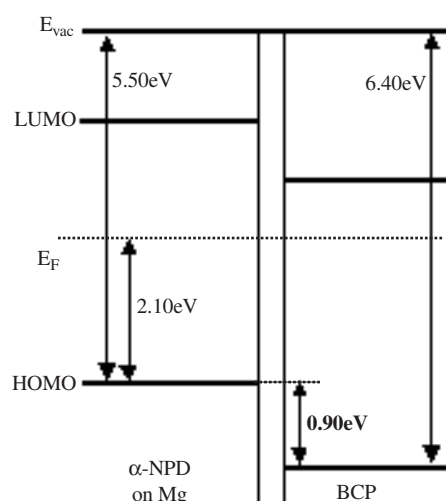


Figure 9. The electronic structure of the undoped α -NPD/BCP interface on Mg (the Mg work function is 3.65 eV).

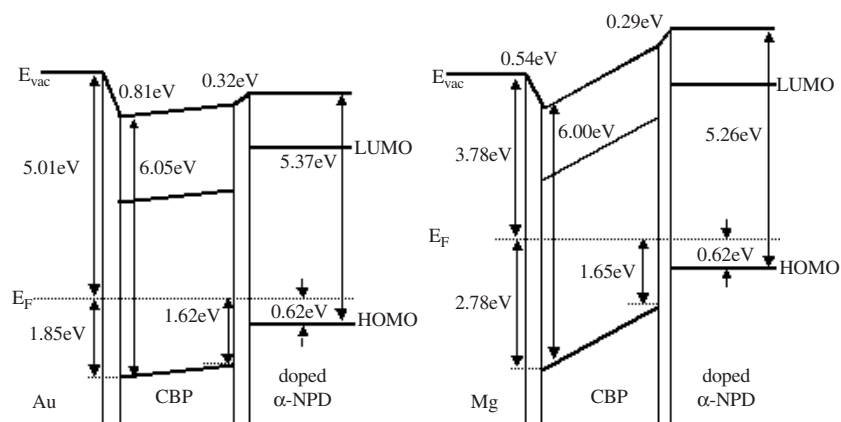


Figure 10. The electronic structure of the OO interface formed by depositing doped α -NPD on CBP on (a) Au and (b) Mg.

interface, and lead to the formation of the observed dipole. The density of charges necessary to establish a 0.5 eV dipole can be estimated to be $5.5 \times 10^{12} \text{ cm}^{-2}$, based on Gauss's law and assuming a dielectric constant of 3, and a molecular spacing of 15 \AA across the interface. This density is too small to be observed via UPS. It corresponds to about 3% of the molecular surface density, suggesting that these states may be related to dopants. The exact mechanism, however, remains unclear and is undergoing further investigations.

6. Summary

This short review summarizes basic results concerning the impact of electrical doping on the energetics of interfaces of π -conjugated molecular films. The p doping of hole transport materials is achieved by insertion of strong electron acceptor molecules such as F_4 -TCNQ in the

organic matrix. Doping occurs by direct electron transfer between the host HOMO and dopant LUMO. At metal/organic interfaces, p doping results in a situation that is analogous to that obtained at inorganic semiconductor interfaces. The position of the molecular levels (HOMO, LUMO) with respect to the metal Fermi level is governed by organic/metal interactions and remains largely independent of the doping (Fermi level pinning). A depletion region is formed in the organic film. When the dopant concentration is high enough for the width of the region to be of the order of 10 nm, an enhancement of several orders of magnitude in injection current, due to hole tunnelling, is observed. Organic/organic interfaces are different in the sense that doping of one of the two materials induces a significant change in molecular level alignment. Whereas vacuum level alignment is observed across most undoped OO interfaces, doping leads to charge exchange with formation of an interface dipole. At this point in time, doping of organic molecular films still requires considerable work, in particular as regards finding efficient and stable n-type molecular dopants. There is little doubt, however, that electrical doping of organic films will play a significant role in lowering drive voltages and controlling transport in more efficient organic devices.

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