Metal-dependent charge transfer and chemical interaction at interfaces between 3,4,9,10-perylenetetracarboxylic bisimidazole and gold, silver and magnesium

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Abstract

Ultraviolet photoelectron spectroscopy (UPS) is used to investigate interfaces between the organic semiconductor 3,4,9,10-perylenetetracarboxylic bisimidazole (PTCBI) and Mg, Ag and Au. The metals span a range of work function and reactivity that leads to the formation of three different types of interfaces. The PTCBI-on-Au interface is abrupt and unreacted, and the relative position of energy levels across the interface precludes charge exchange and occupation of gap states. The lower work function of Ag leads to a metal-to-organic charge transfer and formation of polaron-like states at the PTCBI-on-Ag interface. Finally, the PTCBI-on-Mg interface shows clear evidence of a strong chemical interaction, which alters the electronic structure of the organic molecules at the interface and results in the formation of a different type of gap states. Dipole barriers consistent with the energetic and chemical characteristics of each interface are seen in all three cases. Finally, the three interfaces exhibit nearly identical Fermi level positions with respect to the organic highest occupied and lowest unoccupied molecular orbitals. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the challenging technological issues in the development of devices based on small conjugated organic molecules or polymers is the fabrication of contacts leading to efficient, i.e. low voltage, and stable electron and hole injection into these materials. To help address this issue, a growing body of work has emerged in which photoelectron spectroscopies have been used to investigate the energetics of molecular levels and the chemical interactions at metal–organic semiconductor interfaces, with the goal of understanding the processes governing the injection of charges into molecular semiconductors. Over the past few years, these studies have demonstrated that metal–organic interfaces are more complex than originally anticipated. In particular, they showed that the common assumption of vacuum level alignment, which is the analog of the Schottky–Mott limit for inorganic semiconductors and was believed to be valid at weakly interacting

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interfaces such as metal/organic interfaces, was mostly incorrect [1–3]. It was found instead that interface dipole barriers as large as 1–1.5 eV did exist and did affect significantly the magnitude of the charge injection barriers [3–7]. Furthermore, investigations of a variety of such interfaces revealed a wide range of interface chemical interactions, which were shown to depend not only on the specific chemical elements brought together at the interface, but also on the sequence and method of formation of these interfaces. Finally, these investigations revealed a range of electronic behaviors [3], whereby the dependence on the metal of the Fermi level position in the semiconductor gap did vary considerably from one organic material to the next. At this point, however, a number of questions remain unanswered. The origins of the interface dipoles, which have been variously attributed to charge transfer across the interface [1–3], polarized chemical bond formation, and the effect of the electronic image force outside a metal surface [6,8], is still uncertain, and the role played by interface chemical products and chemistry-induced interface electronic states in the carrier injection process is still unclear. Given the diversity of metal/organic systems, experiments involving the systematic variation of a small number of interface parameters appear therefore to be necessary to finally reach a predictive understanding of these interfaces.

We present in this paper a study of interfaces formed by depositing the organic semiconductor, 3,4,9,10-perylenetetracarboxylic bisimidazole (PTCBI) on three metals: Au, Ag and Mg. The trans-isomer of PTCBI, a derivative of the well-studied 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) molecule, is represented in the inset of Fig. 1. It differs from PTCDA by the transformation of one carboxylate moiety of the anhydride into an imidazole group on each end of the molecule. PTCBI was recently used as a central photoactive layer in a high efficiency organic solar cell [9]. From the viewpoint of our interface studies, this organic molecule is interesting because of its presumed large ionization energy and electron affinity, and the direct comparison it affords with the well-studied PTCDA. The three metals were chosen because of their different reactivities and
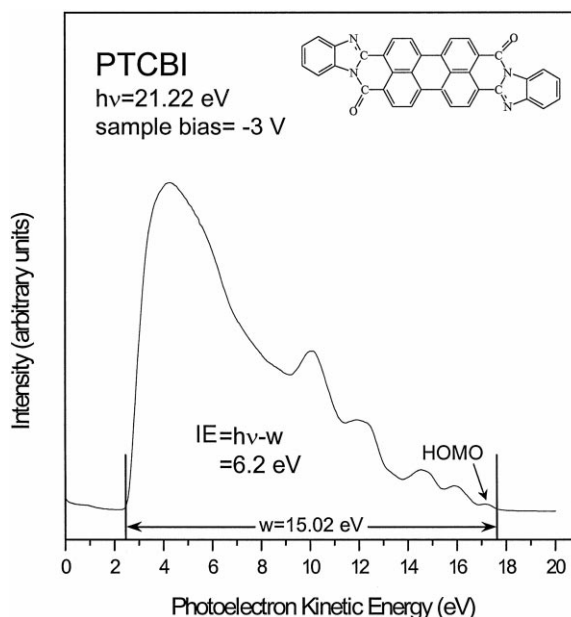

Fig. 1. He I spectrum of clean PTCBI. Inset: chemical structure of the PTCBI molecule.

their span of work functions (from 3.7 eV for Mg to ∼5 eV for Au), which presumably extend from below to above the electron affinity of the organic material. Indeed, we show that the three interfaces exhibit marked differences in the direction of the metal–organic charge exchange, and in the chemical interactions across the interface. These differences shed light on the relationship between chemical structure and electronic property of metal–organic interfaces.

2. Experiment

The deposition of all the metal and organic films and the ultra-violet photoemission spectroscopy (UPS) measurements were done in two interconnected ultrahigh vacuum systems, allowing measurements on pristine surfaces. Prior to insertion into the vacuum system, the PTCBI was purified via three cycles of gradient sublimation. The depositions were done in a sample preparation chamber, with a base pressure of 4×10^{-10} Torr, while the UPS measurements were performed in an analysis chamber with a base pressure of 5×10^{-11}

Torr. The analysis chamber was equipped with a He discharge lamp providing both He I (21.22 eV) and He II (40.8 eV) radiation for UPS and a double-pass cylindrical mirror analyzer. The overall energy resolution of the UPS system was 0.150 eV, as determined from the width of the Fermi edge on a freshly deposited Au surface.

The interfaces were formed by depositing the organic material on freshly deposited metal films. The Fermi level position and work function of each metal film was determined first. The organic layer was then incrementally deposited on the clean metal surface, and spectroscopic data were collected at each thickness. The incremental deposition was continued until the substrate signal was undetectable in the UPS measurement, and the data were, therefore, representative of the clean organic material. In accord with the convention established in previous work [1–7], the ionization energy of the organic film was determined by taking the difference between the vacuum level position, measured using the onset of photoemission, and the top of the highest occupied molecular orbital (HOMO) defined as the intercept between the tangent to the low binding energy edge of the organic HOMO and the background level. The onset of photoemission and vacuum level position were measured with a –3 V bias applied to the sample to raise its energy level structure and clear the vacuum level of the cylindrical mirror analyzer.

3. Results

A typical UPS spectrum of clean PTCBI is presented in Fig. 1. The spectrum consists of a broad, low-energy secondary electron peak, which results from inelastically scattered electrons, and several well-defined density of states related features, the highest kinetic energy (lowest binding energy) of which we attribute to the PTCBI HOMO. The low-energy edge of the secondary electron peak corresponds to the vacuum level of the sample. The ionization energy of the material (IE) is measured in a standard way, i.e. the photon energy minus the total width of the PTCBI spectrum, measured from the low-energy onset to the
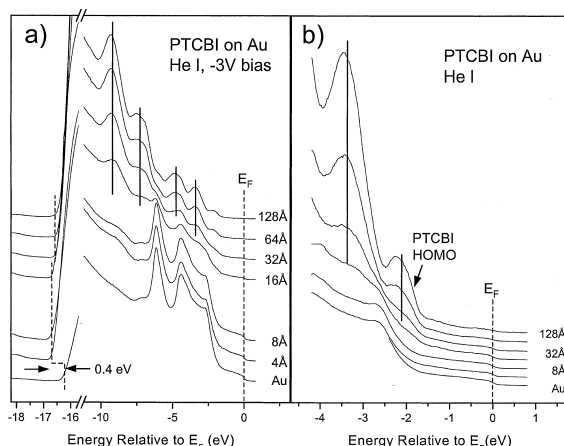

Fig. 2. (a) He I spectra of interfaces formed by incremental deposition of PTCBI on Au. (b) Top of the valence density of states at the PTCBI/Au interface. Vertical lines are intended as guides to the eye.

high kinetic energy edge of the PTCBI HOMO, as illustrated in Fig. 1. We find the IE to be 6.2 ± 0.1 eV, which is ~0.5 eV smaller than that of PTCDA [3,10].

Figs. 2(a) and (b) show the full valence spectrum and the HOMO energy region collected using He I radiation for several nominal thicknesses of PTCBI deposited on Au. Referring to Fig. 2(a), we see evidence that the sticking coefficient of PTCBI on Au is less than unity. The probing depth of UPS is only a few angstroms, but the Au substrate feature at ~–7 eV is still clearly visible at a nominal coverage of 32 Å, indicating that either the actual coverage is less than this value, or the organic material forms islands on the Au surface. Both scenarios result from a weak organic–substrate interaction. Despite the actual coverages being less than the assumed values, a nominal coverage of 4 Å results in the low-energy onset of photoemission (vacuum level) shifting to lower energy by ~0.4 eV. This shift is attributed to an interface dipole, as we have argued previously [2,3], given that the concept of "band bending" has no meaning on this thickness scale. The origin of the dipole will be discussed in Section 4.

The hypothesis of weak interaction between the Au substrate and PTCBI overlayer is supported by the evolution of the organic spectral features. Figs. 2(a) and (b) show that the intensities of the

HOMO and higher binding energy features increase with increasing overlayer thickness without binding energy shift, rigid shift or shift of the molecular features relative to one another. Furthermore, no additional states, e.g. gap states of the type seen at interfaces like Mg, Li, K or Ca on Alq$_3$ [11–13], or In and Sn on PTCDA [10,14] are observed. Such states generally indicate either strong chemical interaction, or charge transfer at the organic–substrate interface. It should be pointed out that if PTCBI clusters on the Au surface, molecules at the metal/organic interface might not be readily detected in UPS. Nevertheless, the lack of additional states at the lowest coverage investigated is a good indication of a lack of strong organic/metal interaction.

The binding energy of the top of the PTCBI HOMO relative to the Au Fermi level (the hole injection barrier) is 1.6 ± 0.1 eV, which is almost as large as the optical absorption gap (1.7 eV) of the organic material [9]. Although the transport gap is presumably higher due to excitonic effects, the PES result suggests that, as for PTCDA [10,14], the interface position of the Fermi level is relatively close to the PTCBI lowest unoccupied molecular orbital (LUMO).

The He I UPS spectra of the interface formed by deposition of PTCBI on Ag are presented in Figs. 3(a) and (b). In this case, the substrate features are completely eliminated at a nominal organic film thickness of 16 Å, suggesting that the PTCBI coverage is higher and/or more homogeneous than for an equivalent deposition on Au, a result of the stronger organic-substrate interaction. The evolution of the vacuum level position is also different than in the previous case (left part of Fig. 3(a)). Initially, the vacuum level shifts toward higher kinetic energy by about 0.2 eV at 4 Å. It shifts in the same direction by an additional 0.1 eV between 8 and 16 Å. The sign of the shift is opposite to that observed at the Au-PTCBI interface, suggesting a dipole corresponding to an electronic charge transfer from the Ag to the PTCBI. Fig. 3(b) also shows that the HOMO, which peaks at a binding energy of ∼2.4 eV relative to the Fermi level, is visible at the lowest PTCBI coverage, and like all the other PTCBI features, increases in intensity without any binding energy shift. The en-
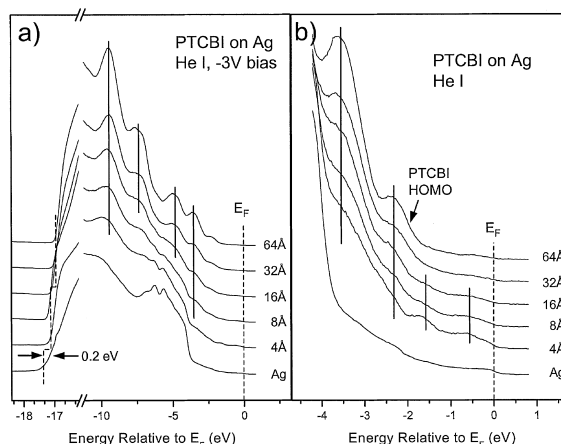

Fig. 3. (a) He I spectra of interfaces formed by incremental deposition of PTCBI on Ag. (b) Top of the valence density of states at the PTCBI/Ag interface. Vertical lines are intended as guides to the eye.

ergy difference between the Fermi level and the leading edge of the HOMO is 1.7 ± 0.1 eV, very close to the previous result. Unlike for PTCBI/Au, however, two additional spectral features are observed at low coverage in the PTCBI gap at ∼1.6 and 0.6 eV below the Fermi level, which cannot be attributed to the substrate, although their intensity decreases with increasing coverage. These states represent molecular orbital states that are only present near the Ag-PTCBI interface, and will be discussed in Section 4.

Figs. 4(a) and (b) show the UPS data corresponding to PTCBI deposited on Mg. These data present similarities with those obtained for PTCBI on Ag: new states appear in the PTCBI gap at low coverage, and bulk-like valence states are obtained for organic film thicknesses as low as 32 Å. However, the vacuum level position and the binding energy of various spectral features as a function of PTCBI thickness behave differently. The vacuum level does not shift as abruptly at this interface as at the previous two. A plot of its position as a function of overlayer thickness (Fig. 5(b)) shows a continuous increase up to 32 Å followed by stabilization. Also plotted are the energy shifts of various spectral features relative to their position at the lowest coverage at which they can be identified. The general trend of increasing energy of the spectral features, concomitant with the
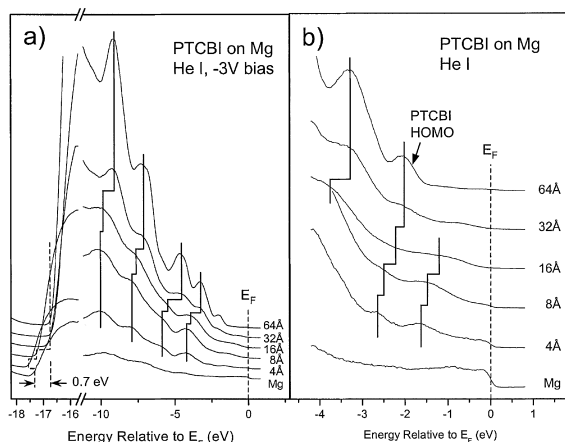
Fig. 4. (a) He I spectra of interfaces formed by incremental deposition of PTCBI on Mg. (b) Top of the valence density of states at the PTCBI/Mg interface. Vertical lines are intended as guides to the eye.

shift of the vacuum level, is too slow to represent final state effects, and closely resembles traditional inorganic semiconductor band bending. Yet, the magnitude of these shifts over the observed length scale would require an enormous net charge density in the organic film: a 1 eV shift over 10 Å would require a net charge density of more than 10^{20} cm^{-3}, or more than 10% of the PTCBI molecules to be negative molecular ions. It is also interesting to note that the molecular level shifts displayed in Figs. 5(a) and (b) are not equal, with discrepancies far greater than our experimental uncertainty of 0.1 eV. Finally, the energy difference between the Fermi level and the HOMO at the PTCBI/Mg interface is 1.6 ± 0.1 eV, nearly indistinguishable from the previous cases, in spite of the more than 1 eV span in the work function of the substrates.

4. Discussion

The analysis of the Au–PTCBI interface is straightforward, when taken in the context of previous studies of metal–organic interfaces [1–7]. There is no evidence of a strong chemical interaction between the substrate and the organic material. The binding energies of the PTCBI spectral features relative to one another are fixed – that is, the energy spacing between levels does not vary with the organic film thickness (Fig. 6). There is an interface dipole, which lowers the organic vacuum level with respect to that of the substrate metal and precisely compensates for the difference between IE (PTCBI) and the sum of the Au work function and the hole barrier (Fig. 7). Electron transfer from the organic to the metal, consistent with the fact that the electron affinity of the organic material is smaller than the substrate work function, would produce a dipole in this direction. However, the lack of free carriers in organic molecular materials like PTCBI leads to the consideration of other origins. The dipole may result from: (i) the electronic image force above the metal surface, which tends to polarize the first organic layer [2,8]; (ii) the organic layer disrupting the metal electron distribution, which tails into the vacuum at a metal surface, thereby effectively reducing the
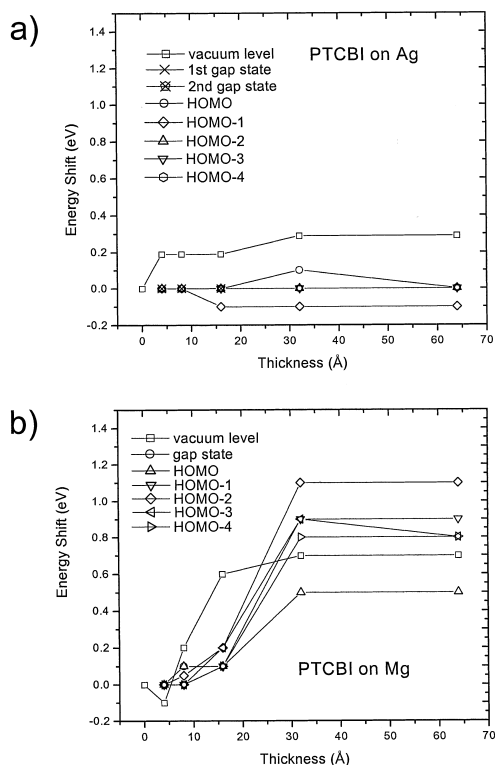

Fig. 5. Kinetic energy shifts of the spectral features as a function of overlayer thickness at the (a) PTCBI/Ag and (b) PTCBI/Mg interface.
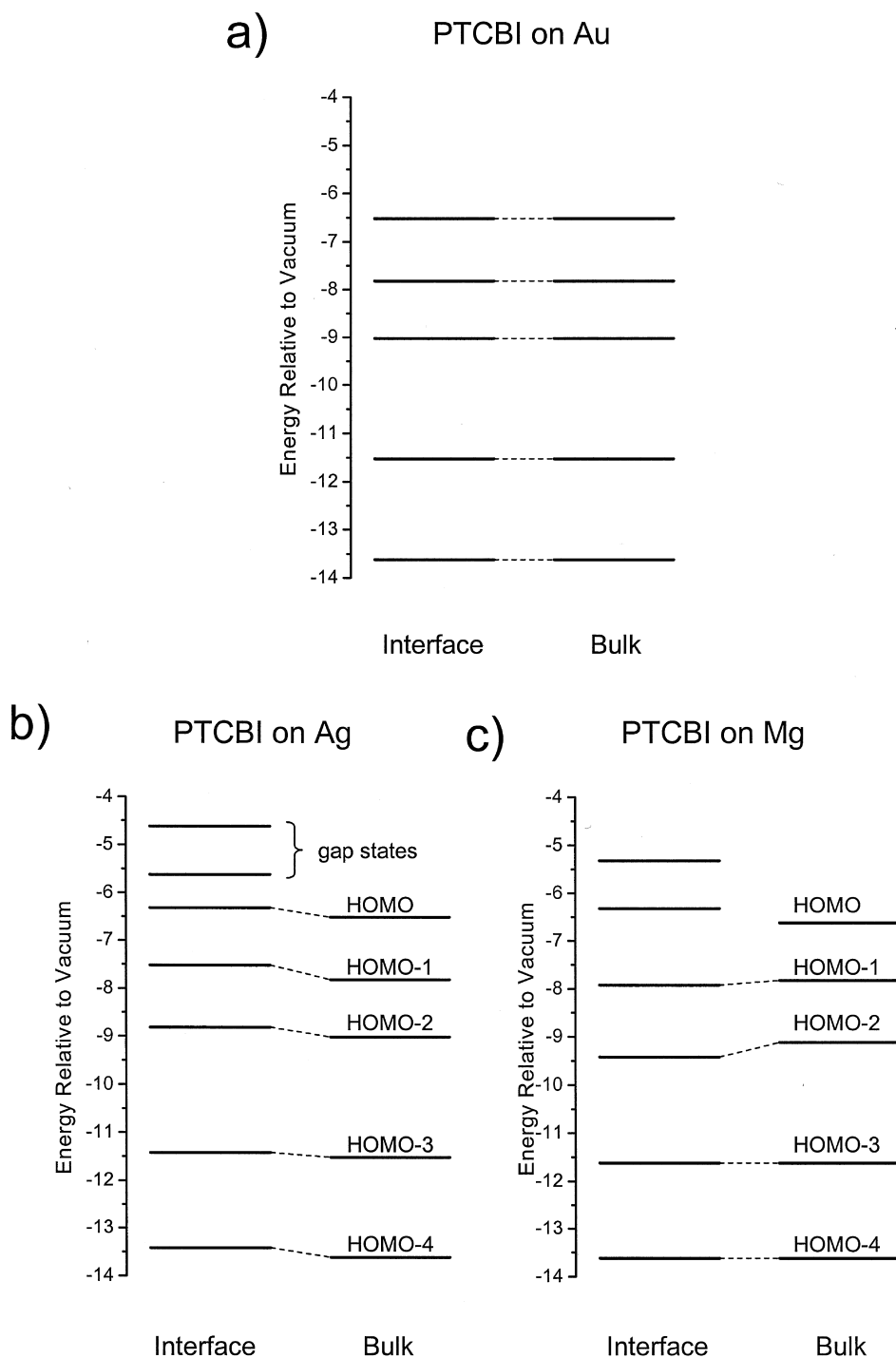
Fig. 6. Binding energy relative to the vacuum level of the interfacial and bulk molecular features at the (a) PTCBI/Au, (b) PTCBI/Ag and (c) PTCBI/Mg interface. The *interface* binding energy is recorded at the lowest coverage for which molecular features are clearly identifiable, i.e. 16 Å on Au, 4–8 Å on Ag and 4 Å on Mg. The *bulk* values correspond to the maximum coverage investigated.
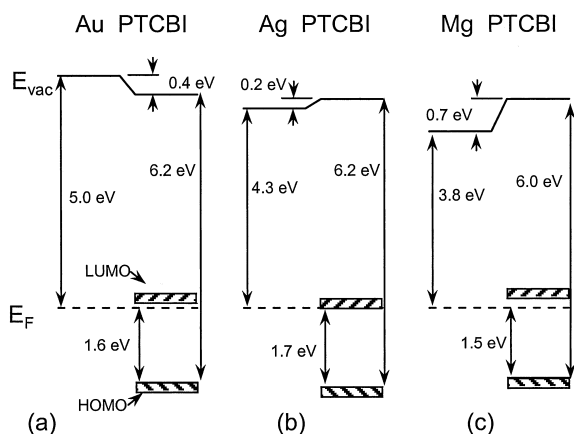
Fig. 7. Molecular energy level alignment diagrams for the (a) PTCBI/Au, (b) PTCBI/Ag and (c) PTCBI/Mg interfaces. For the latter two, the organic levels represent those measured for thicknesses larger than 32 Å, where the gap states are no longer observed.

work function of the substrate [8]; (iii) the polarization of the PTCBI–Au interface bond with electron displacement from the organic to the electronegative metal. Note that the weak chemical interaction and the dipole sign are consistent with previous studies of the reaction products of Au^+ ions with organic molecules [15], where the interaction of the Au cation with a benzene molecule was found to be weak, resulting in either a weak $Au-(C_6H_6)^+$ π-complex, or simple charge exchange $(Au + (C_6H_6)^+)$. The latter scenario (electron transfer from the benzene molecule to the metal), if it were to occur at a solid metal surface as in our experiment, would result in an interfacial dipole of the orientation observed here. The present system is, of course, much different from that described above, which consists of a single metal atom interacting with a single organic molecule. The parallel between the two, however, is instructive and helps rationalizing the interface interaction.

Like PTCBI/Au, the PTCBI/Ag interface displays no evidence of strong chemical interaction. Bauschlicher et al. [16] have studied the interaction of transition-metal ions with benzene using theoretical methods. They find that the Ag^+ ion forms a weak π-complex. The optimized structure consists of a virtually undisturbed benzene ring with

the Ag^+ ion relatively far from the C atoms. Thus, the aromaticity of the benzene ring is not disturbed, consistent with our observations of bulk PTCBI-like molecular features at the lowest coverages and with the fact that molecular level separations remain constant ± 0.1 eV as a function of film thickness (Figs. 5 and 6). Unlike the previous case, however, the PTCBI–Ag interface exhibits a dipole orientation corresponding to an upward movement of the vacuum level upon deposition of the organic layer (Fig. 7). Dipoles of this orientation are uncommon, but have been reported at interfaces between low work function metals and high electron affinity organics, such as PTCDA [3–5] and DP-NTCI (*N*,*N'*-diphenyl-1,4,5,8-naphthyltetracaboxylimide) [1,2,6]. They correspond presumably to an electron transfer from the metal to the molecule, consistent with the fact that the PTCBI electron affinity is much closer to the work function of the substrate than in the previous case. The occupation of the gap states on interface PTCBI molecules, which is discussed below, is consistent with this interpretation.

The third interface displays clear evidence of a strong chemical interaction between the PTCBI and the substrate, consistent with the fact that the chemical interaction between Mg and organic materials is different from that of the previous two metals [17]. Compounds formed by reacting Mg with anthracene have been investigated for their use as reagent in a number of metallic Mg reactions. When Mg is reacted with anthracene in tetrahydrofuran, it reacts with the central ring of the molecule, bonding covalently with two opposite C atoms. Thus, the C–Mg–C bonding bridges the central ring, perpendicular to the long axis of the anthracene molecule. This bonding rehybridizes the two C atoms, causing the molecule to fold by 41° along the line joining the two C atoms [17]. This bonding strongly disturbs the π system of the central ring, and thus alters the aromaticity of the entire molecule. The molecular levels of this compound are expected to differ significantly from that of the original anthracene molecule. By analogy, we believe that a similar reaction with the carbon ring structures of PTCBI may explain the differences in the energy levels observed at low coverages on the Mg/PTCBI interface (Fig. 6). It is

likely as well that the Mg reacts with the remaining carboxyl oxygen and/or the nitrogen of the imidazole group.

The movement of the vacuum level at the PTCBI/Mg interface (Figs. 4(a) and 5) must be examined in light of definitions of "band bending" and interface dipoles. We use the term "band bending" not to imply the existence of delocalized bands, but rather to refer to the electrostatic shifting of energy levels by a net charge density, such as in the depletion region of a crystalline inorganic semiconductor device. We typically speak of an interface dipole when the net charge density, or equivalently the separation of charges, is a result of polarization of the first organic molecular layer at the interface, or chemical bonding between this layer and the substrate. In inorganic systems, "band bending" usually refers to energetic shifts occurring on much longer length scales. In fact, in considering "band bending", the usual assumption is made that the characteristic length scale is much larger than the interatomic (or intermolecular) spacing, such that the material and net charges can be treated as a continuum and the specifics of the interatomic (intermolecular) interactions can be ignored [18]. At the Mg–PTCBI interface described above, we see a systematic shift of the energy levels occurring on a length scale of ∼30 Å. This is larger, but not significantly larger, than a single molecular layer thickness. It is obvious that the existence of discrete molecules cannot be ignored on this length scale, and that the charge distribution cannot be considered as a constant throughout the film as in the typical treatment of "band bending". We therefore conclude that this shift – although it may in fact occur within the first couple of molecular layers – is better described as an interface dipole than as "band bending" (Fig. 7).

The "gap states" observed at low coverage above the PTCBI HOMO may be viewed in two ways: (i) as the result of electron transfer from the substrate metal to the organic; (ii) as energy levels characteristic of a distorted molecular species which results from the reaction of the PTCBI with the metal. Such states have been observed previously at interfaces like In or Sn on PTCDA [10, 14], and Mg, Ca or Li on Alq$_3$ [11–13]. When viewed as the result of simple electron exchange, these states are often referred to as polaron (singly occupied) or bipolaron (doubly occupied) levels. Since the polaron level is singly occupied, and therefore represents a half-filled orbital, it should occur near the Fermi level in equilibrium. However, because organic molecules represent small systems with localized charge carriers, the Coulomb repulsion between the first and second electrons placed in this orbital results in the opening of a Coulomb gap, such that the singly-occupied polaron level will occur below the Fermi level. In our assignment of interfacial energy levels, we attribute the spectral features observed at the Mg–PTCBI interface to characteristic molecular levels of an organometallic compound of Mg and PTCBI. At the Ag–PTCBI interface, on the other hand, the two levels which peak above the PTCBI HOMO at ∼0.6 and ∼1.6 eV below the Fermi level are attributed to bipolaron-like and polaron-like states, respectively. The existence of these states implies the presence of negative molecular ions near the interface, which are the result of electron transfer from the Ag surface to the PTCBI molecules. These ions create the region of net electric field near the interface, which is responsible for the offset of the vacuum level. The interface dipole raises the energy levels of the organic materials with respect to the substrate Fermi level until a detailed balance of charge transfer between the metal and PTCBI is achieved. Referring to Fig. 6, we see that the energies, relative to the vacuum, of the gap states are significantly different at the Mg and Ag/PTCBI interfaces. The gap states at the Mg/PTCBI interface are ∼0.7 eV more tightly bound than those at the Ag/PTCBI interface, supporting their different origins (interfacial chemistry versus simple charge transfer). Finally, it should be noted that in the case of PTCBI on Au, the metal work function is significantly larger than the electron affinity of the organic material. This prevents the charge transfer and formation of polaron states, in accord with the absence of interface gap states (Fig. 2(b)).

The energy level alignment diagrams presented in Fig. 7 are compiled from the data presented in Figs. 2–4. For the cases of PTCBI on Ag and Mg, where gap states exist at the lowest coverages, the

diagrams have been drawn using the binding energies of the spectral features at coverages of 32 Å, where only bulk-like PTCBI features are observed. We note that, very much like the interfaces between metals and PTCDA [3,10,14], the Fermi level appears to be pinned, within our experimental uncertainty, at 1.6 ± 0.1 eV above the PTCBI HOMO. We would therefore predict efficient injection of electrons from all three metals into the LUMO of PTCBI. In the context of the above discussion of interface dipoles versus "band bending", we have interpreted the energy difference between the vacuum levels of Mg and the 32 Å film of PTCBI on Mg as the magnitude of the dipole at this interface. Because the Fermi level is essentially pinned at each of these interfaces, we see that the difference in interface dipoles (Δ) at the three interfaces are essentially equal to the differences in work functions of the substrate metals:

$$|\Delta_{Au} - \Delta_{Ag}| = 0.6 \pm 0.14 \text{ eV} \quad \text{and} \quad |\Delta_{Ag} - \Delta_{Mg}| = 0.5 \pm 0.14 \text{ eV}.$$

5. Summary

In the context of the above discussion, we arrive at the following descriptions of the three interfaces studied. Very different processes are responsible for the formation of the three interfaces, and the resulting alignment of energy levels. PTCBI, when deposited on Au, does not react with the substrate and resembles the unperturbed molecule even at the lowest coverages. PTCBI deposited on Ag interacts more strongly with the substrate, and electron transfer from the Ag to the PTCBI results in the formation of negative molecular ions near the interface, and possibly a weak Ag π-complex. PTCBI deposited on Mg interacts very strongly with the substrate metal, resulting in chemical bonding between the organic and the substrate, which alters the structure of the molecule at the interface, and hence the molecular orbital levels observed.

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