

Organic semiconductor heterointerfaces containing bathocuproine

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The four organic–organic heterointerfaces formed by depositing the organic semiconductor bathocuproine on tris(8-hydroxy-quinoline)aluminum (Alq₃), *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4'' diamine (α -NPD), 4,4'-*N,N'*-dicarbazolyl-biphenyl (CBP), and copper phthalocyanine (CuPc) have been studied using ultraviolet photoelectron spectroscopy. The relative positions of the vacuum levels and highest occupied molecular orbital levels of the organics were measured at each interface. Within our experimental uncertainty of 100 meV, the vacuum levels were found to align at all four interfaces. © 1999 American Institute of Physics. [S0021-8979(99)04520-X]

I. INTRODUCTION

Prior to the use of ultraviolet photoelectron spectroscopy (UPS) to investigate molecular-level alignment at organic–organic heterointerfaces, it was widely assumed that the vacuum levels of two organic semiconductors would align at the interface. When two materials are brought into contact, the Fermi levels must align if the system is in thermodynamic equilibrium. In general, vacuum-level alignment, therefore, requires that the Fermi level be free to move in at least one of the two materials, because of the different positions of the Fermi levels relative to the vacuum in the two isolated materials. In the case of organic molecular semiconductors, vacuum-level alignment was justified by citing the closed-shell nature of the individual molecules, the resulting weak intermolecular bonding, and the lack of interface states within the semiconducting gaps. The Fermi level would be free to move, and the vacuum levels should align. In such a case, the offset between the two organic highest occupied molecular orbitals (HOMOs) would simply be equal to the difference between the ionization energies of the two organics.

Recent UPS studies have confirmed that the vacuum levels do align at the majority of organic heterointerfaces.^{1–5} Several exceptions have been found, including the interfaces between perylenetetracarboxylic dianhydride (PTCDA) and CuPc,² PTCDA and tris(8-hydroxy-quinoline)aluminum (Alq₃),⁶ Alq₃ and *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1' biphenyl-4,4'' diazine (α -NPD),² and tetracyanoquinodimethane (TCNQ) and tetrathianaphthacene (TTN).³ The formation of a charge-transfer complex, with an electron being donated by the TTN to the acceptor TCNQ, was used to explain the TCNQ–TTN interface dipole.

Such donor–acceptor complexes may be expected at interfaces between materials with large differences in electron affinities. However, this cannot explain all the cases which have been investigated. As noted above, the PTCDA/Alq₃ interface exhibits a measurable dipole, while PTCDA/ α -

NPD does not, despite the smaller electron affinity of α -NPD compared to Alq₃.^{2,7}

In this article, we report the results of an investigation of four organic–organic heterointerfaces. The interfaces were formed by depositing bathocuproine (BCP) on Alq₃, α -NPD, 4,4'-*N,N'*-dicarbazolyl-biphenyl (CBP), and copper phthalocyanine (CuPc). The molecular structures of these materials are presented in Fig. 1. In addition to the fundamental importance of such a systematic study of interfaces between one organic and a range of others, the first three of the above interfaces have recently been used in organic light-emitting devices (OLEDs),^{8,9} and our results, therefore, have obvious technological implications.

II. EXPERIMENT

All experiments were performed in ultrahigh vacuum (UHV). Organics were deposited in a preparation chamber (base pressure 4×10^{-10} Torr), which is connected to the main analysis chamber (base pressure 4×10^{-11} Torr). The UPS system consists of a double-pass cylindrical mirror analyzer and a He discharge lamp. He I (21.2 eV) and He II (40.8 eV) photon energies were used. The overall resolution of the system was estimated to be 150 meV from the width of the Fermi-level step on freshly deposited Au.

Samples were prepared by depositing ≈ 100 Å of a base organic (Alq₃, α -NPD, CBP, or CuPc) on a flat substrate [Si(100):300 Å Cr:1000 Å Au]. All film thicknesses were determined by timed depositions calibrated using a quartz-crystal microbalance. No corrections for sticking coefficients different from unity were used. The base organic was studied using UPS to determine the quality of the film, to measure its ionization energy, and to determine the binding energy of the HOMO with respect to the Fermi level. The position of the vacuum level was determined from the low-energy onset of photoemission with the sample at -3 V bias with respect to the analyzer. Incremental thicknesses of BCP were deposited on the base organic, doubling the total overlayer thickness at each step. UPS spectra were collected at each thickness until the data showed no contribution from the base layer, indicat-

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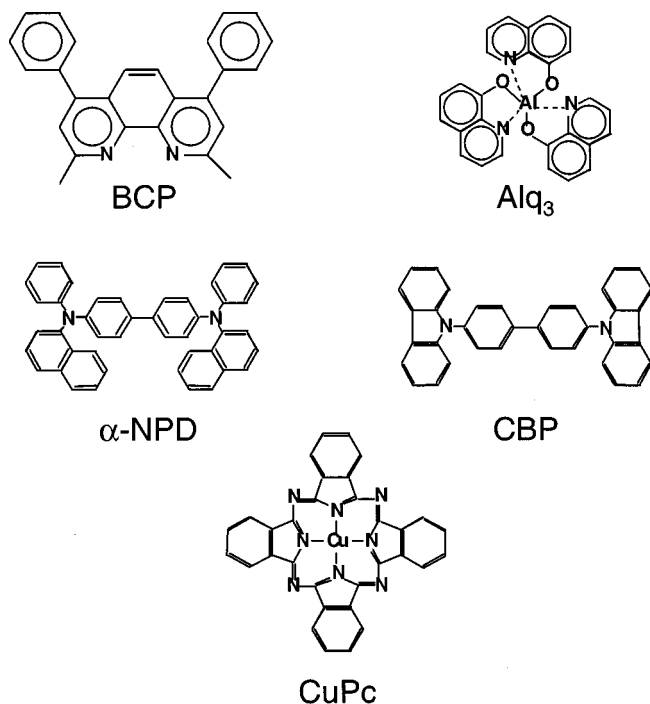


FIG. 1. Molecular structures of the organics used in this study.

ing a saturated overlayer with thickness greater than the probing depth of the UPS technique. The data were then compiled, examined for evidence of overlayer-induced molecular-level displacement, hereafter called “bandbending,” and the HOMO-level offset and interface dipole magnitudes were extracted.

The position of the top of the HOMO was estimated from the zero crossing of the linear extrapolation of the low-binding-energy side of the HOMO spectral peak. In the case of BCP, there appear to be three overlapping peaks which cannot be resolved and form a single, broad spectral feature. This is illustrated in Fig. 2. The distance between the maximum of this feature and the top of the HOMO, as defined above, is 1.75 eV. This fact was used to determine the position of the top of the BCP HOMO at intermediate overlayer thicknesses on heterointerfaces, where the overlap of spectra from two organics obscured the low-binding-energy edge.

The position of the lowest unoccupied molecular orbital (LUMO) has been estimated in each case by adding the energy of the onset of optical absorption to the HOMO level. The position of the transport LUMO will differ from this position for two reasons: (1) the transport LUMO energy will be increased by the electron–electron Coulomb interaction energy, since the electron transport process involves adding an extra electron to a neutral molecule; and (2) the transport LUMO energy will be decreased by molecular relaxation, assuming the residence time of an electron on a molecule is longer than the relaxation time. Although we do not know the exact magnitude of these effects, they are expected to be similar in both organics involved, such that the LUMO–LUMO offset remains \approx to that estimated using the optical absorption gaps.

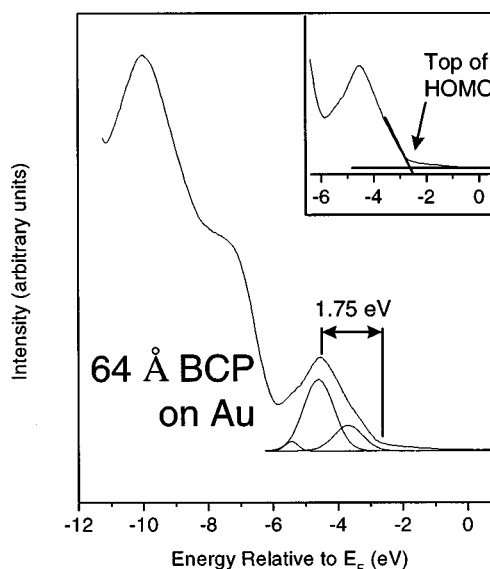


FIG. 2. He I (21.22 eV) UPS spectrum of 64 Å BCP on Au. The lowest-binding-energy feature appears to consist of three peaks (fitted peaks shown below). The distance from the feature maximum to the top of the HOMO is 1.75 eV. Our definition of the top of the HOMO is illustrated in the inset.

III. RESULTS AND DISCUSSION

The UPS data corresponding to the interface formed by depositing BCP on Alq₃ are presented in Fig. 3. The bottom spectrum is characteristic of clean Alq₃, as has been reported elsewhere.⁶ The ionization energy of the Alq₃ was measured to be 5.8 ± 0.1 eV, in excellent agreement with earlier work.⁶ The initial deposition of 4 Å BCP on the clean Alq₃ surface results in a rigid shift of 50 meV towards higher binding energies, indicating a slight overlayer-induced bandbending in the Alq₃ layer. After deposition of 16 Å of BCP, the UPS spectra resemble those of BCP on Au, and the Alq₃ features

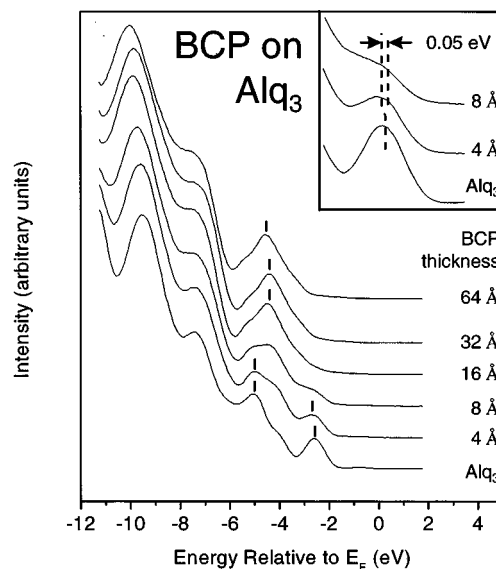


FIG. 3. He I (21.22 eV) UPS spectra of BCP on Alq₃. Tick marks are included as a guide to the eye. The inset shows the Alq₃ HOMO at low coverages, illustrating the slight bandbending observed.

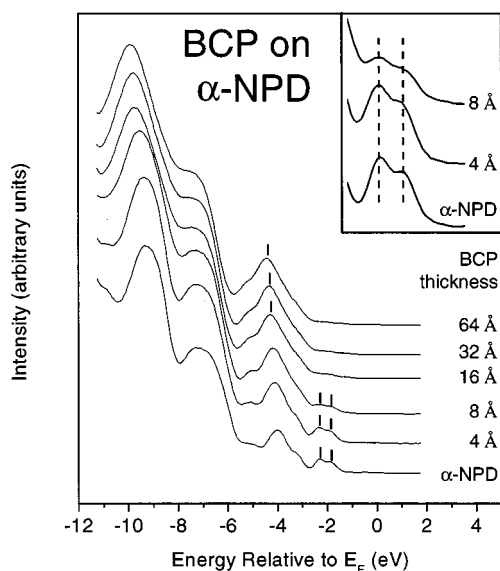


FIG. 4. He I (21.22 eV) UPS spectra of BCP on α -NPD. Tick marks are included as a guide to the eye. The inset shows the α -NPD HOMO position at low coverages.

are completely suppressed, indicating that the Alq₃ layer is completely covered at this thickness. Further deposition of BCP results in a slight (100 meV) shift towards higher binding energies, which may be a result of bandbending in the BCP layer, or may indicate charging within the wide-gap material. The ionization energy of the BCP film was 6.4 ± 0.1 eV. By removing the contributions of bandbending from the HOMO–HOMO offset, the hole-transport barrier at this interface was determined to be 0.65 ± 0.1 eV, with the HOMO level of Alq₃ being above that of BCP, as illustrated in Fig. 7. The LUMO levels, estimated using the optical absorption gaps of 2.7 and 3.5 eV for Alq₃ (Ref. 10) and BCP,¹⁰ respectively, predict a small electron-transport barrier of 0.15 ± 0.1 eV from Alq₃ to BCP. The onset of photoemission (not shown) was used to determine the position of the vacuum level at each thickness. The only movement observed was attributed to the above-mentioned bandbending/charging effects. The vacuum levels, therefore, align at this interface, within our experimental uncertainty of ± 0.1 eV.

This interface has recently been used in high-efficiency electrophosphorescent OLEDs.⁸ A thin layer of BCP was inserted between two layers of Alq₃—one used purely as an electron-transport layer, and the other as a doped luminescent layer. The purpose of the BCP was to confine holes within the luminescent layer, which is reasonable considering the 0.65 eV hole barrier measured here. Additionally, for this scheme to be efficient, electrons must be transported from Alq₃, across the BCP layer, and into the Alq₃ luminescent layer. This requires near-alignment between the Alq₃ and BCP LUMO levels at the interfaces. The LUMO–LUMO offset estimated above is very small, and therefore, consistent with the measured device performance.

Depositing BCP on the clean surface of α -NPD does not result in any appreciable bandbending within the α -NPD layer, as shown in Fig. 4. The spectral features of the clean α -NPD surface, and the measured ionization energy of 5.4

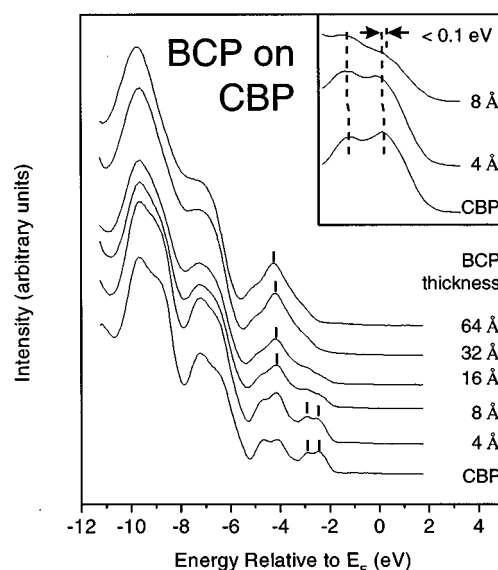


FIG. 5. He I (21.22 eV) UPS spectra of BCP on CBP. Tick marks are included as a guide to the eye. The inset shows the CBP HOMO position at low coverages.

± 0.1 eV are in excellent agreement with previously reported values.¹ Increasing BCP thickness results in the attenuation of the α -NPD HOMO spectral intensity. It is difficult to identify the BCP HOMO at intermediate thicknesses, because of the similarity in shape between the BCP and α -NPD features at the BCP HOMO binding energy. However, at 16 Å BCP, where the α -NPD HOMO is completely attenuated, we can unambiguously identify the BCP HOMO. Further deposition of BCP results in a 200 meV shift of the spectral features towards higher-binding energy, much as was observed for BCP on Alq₃. The ionization energy of the BCP film was 6.5 ± 0.1 eV. Once again, the vacuum levels align at the interface, within 0.1 eV. After subtracting the contribution from BCP bandbending, the HOMO–HOMO offset at the interface was found to be 1.0 ± 0.1 eV, with the α -NPD HOMO above that of BCP (Fig. 7). Using the optical absorption band gaps [3.1 eV for α -NPD (Ref. 11)], the electron-transport barrier (LUMO–LUMO offset) was estimated to be 0.6 ± 0.1 eV, with the LUMO of α -NPD above that of BCP.

The UPS spectrum of clean CBP is shown at the bottom of Fig. 5. The ionization energy of the clean CBP film was 6.0 ± 0.1 eV, as previously reported.¹² A slight (< 100 meV) shift of the CBP features was observed upon deposition of 4 Å of BCP. The CBP spectral features are not completely suppressed until a BCP thickness of 64 Å is reached, indicating that the BCP has a lower sticking coefficient on CBP, that is, does not undergo layer-by-layer growth, or that the initial CBP surface was rough, resulting in CBP protruding through the BCP film until the higher film thickness was reached. Little BCP bandbending (< 100 meV) was observed, and the ionization energy of the BCP film was measured to be 6.4 ± 0.1 eV, in agreement with the previous two interfaces. The HOMO–HOMO offset at the interface is 0.44 ± 0.10 eV, with the CBP HOMO above that of BCP (Fig. 7). The LUMO–LUMO offset, estimated using the optical

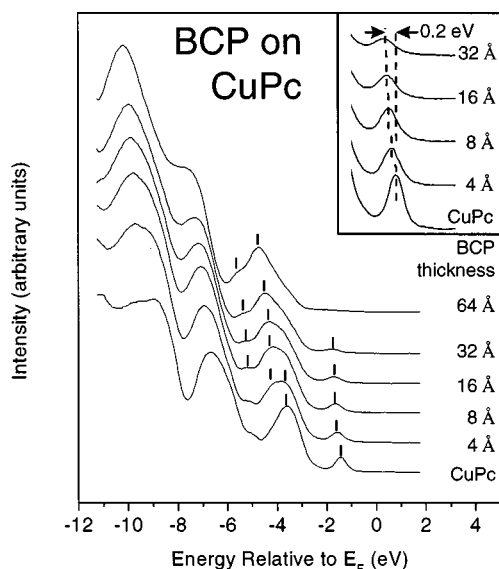


FIG. 6. He I (21.22 eV) UPS spectra of BCP on CuPc. Tick marks are included as a guide to the eye. The inset shows the CuPc HOMO at low coverages.

band gaps [3.1 eV for CBP (Ref. 10)], is 0.04 eV, which is less than our estimated uncertainty of 100 meV. The LUMO levels, therefore, align with our experimental uncertainty. Once again, the vacuum levels were found to align at this interface.

The BCP/CBP interface has also been used in high-efficiency OLEDs.⁸ In this case, the BCP layer was inserted between Alq₃ and the electron-transport layer, and a doped CBP luminescent layer. Again, the purpose of the BCP was to confine holes within the luminescent layer, consistent with our measured hole barrier at this interface. Once again, for this scheme to be efficient, the BCP and CBP LUMO levels must align to allow electron transport into the CBP layer. The LUMO–LUMO offset estimated above is negligible, and therefore, consistent with the measured device performance.

The results of the deposition of BCP on CuPc are presented in Fig. 6. The spectrum of clean CuPc, and its measured ionization energy of 5.2 ± 0.1 eV, agree well with previous studies.¹ The deposition of 4 Å BCP results in an ≈ 200 meV overlayer-induced bandbending towards higher-binding energy within the CuPc film. As in the case of BCP on CBP, the CuPc features were not completely suppressed until a thickness 64 Å was reached. This behavior, indicating a low sticking coefficient, or possibly the growth of islands which coalesce at higher coverage, has been observed at several interfaces containing CuPc.¹ Substantial BCP bandbending of ≈ 300 meV towards higher-binding energy was observed with increasing thickness. The larger degree of bandbending observed here may support the island growth mechanism of BCP on CuPc, as the 64 Å spectrum may, therefore, be sampling the top of islands which are substantially thicker than the nominal coverage, and therefore, exhibit a greater degree of bandbending (or charging). The ionization energy of the saturated BCP film was measured to be 6.5 ± 0.1 eV. After correcting for these effects, the HOMO–

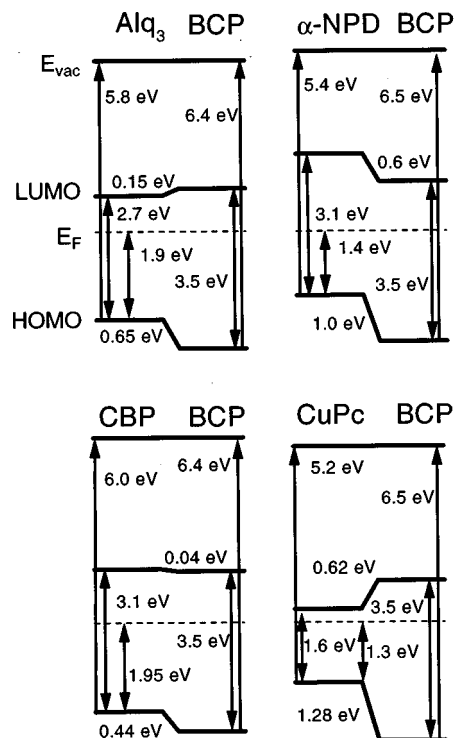


FIG. 7. Molecular-level diagrams summarizing the results of the four organic–organic interfaces. The observed Fermi-level position at each interface is indicated.

HOMO offset at the interface was determined to be 1.28 ± 0.1 eV, with the CuPc HOMO well above that of BCP (Fig. 7). Using the optical gaps [1.6 eV for CuPc (Ref. 10)], the LUMO–LUMO offset is 0.62 ± 0.10 eV, with the CuPc LUMO below that of BCP. As was the case for the previous three interfaces, the vacuum levels were found to align.

Interfaces between BCP and a range of different organics have been presented. These organics span a range of electron affinities from 2.3 eV (α -NPD) to 3.6 eV (CuPc), and ionization energies from 5.2 eV (CuPc) to 6.0 eV (CBP). It is interesting that despite these wide ranges, the vacuum levels were found to align at all interfaces. As far as the electron affinities are concerned, this may be a result of the intermediate value of the BCP electron affinity (3 eV). The difference in electron affinities of the two interface constituents does not exceed 0.7 eV at any of the four interfaces investigated, in contrast to the reported electron affinity differences between 0.8 and 1.5 eV at the Alq₃/ α -NPD, PTCDA/CuPc, and PTCDA/Alq₃ interfaces. This justification appears less reasonable, however, when ionization energies are considered, given that BCP has the largest ionization energy of the group, 1.2 eV larger than that of CuPc. It is clear, in any case, that the Fermi level at each of these organic surfaces is able to move in an energy window sufficient to avoid the formation of a compensating interface dipole.

IV. CONCLUSIONS

UPS studies of four organic–organic heterointerfaces have been reported. The four interfaces were formed by depositing BCP on Alq₃, α -NPD, CBP, and CuPc. The first

three of these interfaces are used in OLEDs. The hole-transport barrier (HOMO–HOMO offset) was measured at each interface. No dipoles were found at these interfaces, implying that the vacuum levels align in all four cases.

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