Photoemission study of frontier orbital alignment at a metal–organic interface as a function of conjugation length of oligothiophene derivatives

A. J. Mäkinen[a)] and I. G. Hill
Optical Sciences Division, Naval Research Laboratory, Washington, DC 20375

T. Noda and Y. Shirota
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka, Japan

Z. H. Kafafi
Optical Sciences Division, Naval Research Laboratory, Washington, DC 20375

We report an ultraviolet photoemission spectroscopy (UPS) study of solid films of two molecules, 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) and 5,5′-bis(dimesitylboryl)-2,2′:5′2′-terthiophene (BMB-3T) which have been characterized as potential electron transport materials in organic light-emitting devices. Using the frontier orbital positions at a metal-organic interface, determined from the UPS measurements, together with the optical band gaps of the molecules, the electron injection barriers for the two oligothiophene derivatives are found to be significantly different. This barrier is estimated to be ~0.2-0.3 eV lower for BMB-2T than for BMB-3T at a metal–organic interface. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1343471]

The efforts to realize a full-color flat panel display utilizing organic light-emitting diodes (OLEDs) have intensified after successful demonstration and commercialization of OLEDs in monochromatic and more recently in three-color displays. One of the critical requirements for achieving a full-color display is the availability of red, green and blue emitters with high efficiency and good thermal stability. Most recently, the focus has been on developing blue-emitting electron-transport materials. Previously investigated materials with these properties for OLED applications include 1,3-bis[4-(N,N′-dimethylamino)phenyl-1,3,4-oxadiazolyl] benzene,[1] and 3-(biphenyl-4-yl)-5-(4-dimethylamino) -4-(4-ethylphenyl)-1,2,4-triazole.[2] However, the glass-forming properties and morphological changes of these materials have not been reported in detail, and hence, there is an ongoing attempt to develop blue-emitting electron-transport materials with good thermal and morphological stability.

In this letter, we report an ultraviolet photoemission (UPS) study of solid films of two molecules, 5,5′-bis(dimesitylboryl)-2,2′ -bithiophene (BMB-2T) and 5,5′-bis(dimesitylboryl)-2,2′:5′2′ -terthiophene (BMB-3T). These materials form amorphous films upon vacuum evaporation with relatively high glass transition temperatures (107 °C for BMB-2T and 115 °C for BMB-3T), and they are characterized as electron-transport materials.[3] Both materials are transparent in the visible region. In addition, they are blue emitters with a peak of the most intense fluorescence bands at 440 and at 488 nm for BMB-2T and BMB-3T, respectively. Most recently, BMB-2T has been used as a blue emitter in an OLED structure.[4] Our UPS results show that the frontier orbital alignment of the oligothiophene derivatives at the metal–organic interface is dependent on the number of thiophene rings present, i.e., the effective conjugation

length of the molecule. The position of these orbitals at the interface together with the transport gap will determine the carrier injection characteristics and the overall performance of a device utilizing these molecules as electron transporters.

The ultraviolet photoemission spectroscopy (UPS) measurements were carried out in a two-chamber UHV system (base pressure 10^{-10} Torr) with a preparation and an analysis chamber separated by a gate valve. The organic materials were synthesized and purified as described in detail elsewhere.[4] The BMB-2T and BMB-3T films were deposited from a resistively heated quartz crucible onto a polycrystalline Ag foil, which was first cleaned by ion sputtering. The contamination levels of the Ag substrate were monitored with x-ray photoemission spectroscopy (XPS). The thickness of the organic overlayers was monitored with a quartz crystal microbalance. After evaporation, the samples were moved from the preparation chamber to the analysis chamber without breaking the vacuum. Photoemission spectra of the films were recorded for HeI ($h\nu = 21.22$ eV) and HeII ($h\nu = 40.82$ eV) radiation using a hemispherical energy analyzer for electron detection. The resolution of the analyzer was set to 50 meV. The sample was biased at -3.0 V to compensate for the contact potential between the sample and the analyzer.

The film deposition was done layer by layer, and the HeI and HeII spectra were recorded for each deposition. The HeI spectra for BMB-2T and BMB-3T films of different thicknesses are shown in Fig. 1 where the binding energy is referenced to the Fermi level (E_F) of the Ag substrate. As the coverage of BMB-2T and BMB-3T is increased, new spectral features due to the molecular orbitals quickly appear at the higher binding energies (>7.5 eV) in the HeI spectra. However, the substrate peaks in the spectra at the intermediate binding energies between 4 and 8 eV do not completely disappear and the highest occupied molecular orbitals (HOMO) are not fully formed until a 16 Å nominal coverage

[a)]Electronic mail: ajm@ccs.nrl.navy.mil
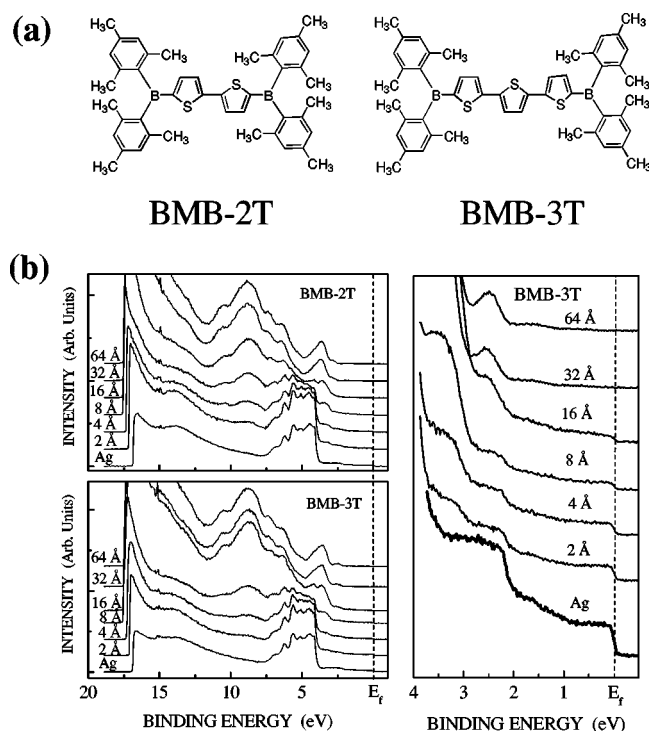
(a)

BMB-2T   BMB-3T

(b)

FIG. 1. (a) The structures of BMB-2T and BMB-3T and (b) HeI spectra of BMB-2T and BMB-3T at various film thicknesses (left panel) and the evolution the HOMO of the BMB-3T film (right panel).
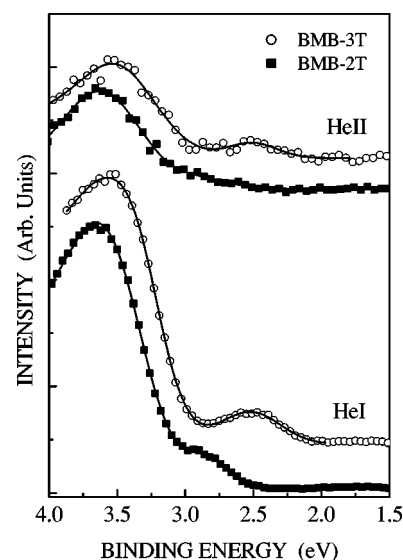

FIG. 2. HeI and HeII spectra of the HOMO levels of BMB-2T and BMB-3T at a 64 Å film thickness. The solid lines indicate a least square fit of a sum of Gaussian functions superimposed on a polynomial background function.

is achieved. E_F is still visible at this coverage, and given the relatively shallow probing depth of UPS (5 Å), we conclude that the substrate is not fully covered by the molecular film. This may be interpreted as possible clustering of the molecules at the substrate surface upon evaporation. We also want to point out that the position of the HOMO does not change after 16 Å, and since the E_F is still visible at this coverage we can be confident that the energy scale remains the same at higher coverages.

Both films show an abrupt shift of the vacuum level at low coverages (≤ 8 Å) after which the level position stays constant with increasing film thickness. This shift is almost identical in both films, 0.56 and 0.53 eV in BMB-2T and in BMB-3T, respectively. This is an indication of a charge dipole layer forming at the metalorganic interface. Since the shift is positive, i.e., there is a shift towards higher binding energies, it implies that the dipole is directed out of the metal surface. The possible mechanisms for the dipole formation include charge transfer between the metal and the organic, chemical reaction and polarization of the molecular layer due to image force effect at the interface.[5,6] We see no evidence for charge transfer between the metal and the organic in our spectra, i.e., there are no midgap states or uniform shifts of the spectral peaks observed in the spectra during the initial stages of film growth. Also, we have performed additional XPS measurements on the films of other similar oligothiophene derivatives deposited on Ag substrates, and we have not found any evidence for a chemical reaction between the metal and the organic.[7] These findings are in agreement with other studies which have found no significant chemical reaction between thiophene and a noble metal (Au).[8] Therefore, the most likely mechanism for dipole layer formation is the polarization of BMB-2T and BMB-3T layers at the interface,

and this mechanism has recently been discussed in detail elsewhere.[9]

The HeI spectra of BMB-2T and BMB-3T in Fig. 1 appear very similar, especially at high binding energies. However, the positions of the highest occupied molecular orbital (HOMO) levels of the two molecules are significantly different as shown in more detail in Fig. 2. The exact position of the HOMO levels was obtained from a least square fit of a sum of Gaussian functions superimposed on a polynomial background function. The peak maxima of the HOMO levels were at 2.82 and 2.51 eV in the BMB-2T and the BMB-3T films, respectively. Remarkably, it is only the HOMO levels of BMB-2T and BMB-3T that are shifted significantly with respect to each other. The positions of the peak maxima of the lower lying HOMO-1 levels of the two films are found to be very close to each other, at 3.55 and at 3.65 eV in BMB-2T and BMB-3T, respectively. The HOMO lines are also observed in the HeII spectra of the two films included in Fig. 2. This eliminates the possibility that the relatively weak HOMO features of the HeI spectrum might be an artifact of the HeII spectrum near the minimum binding energy observed in the HeI spectrum.

The obvious structural difference between the BMB-2T and the BMB-3T molecules is the number of the central thiophene rings. Therefore, it is natural to suspect that the number of the thiophene units will have an effect on the photoemission spectra of the molecules. As a matter of fact, the UPS spectra of BMB-2T and BMB-3T resemble closely the UPS spectra of bithiophene and terthiophene reported in the literature.[10–13] The combination of experimental and computational work has shown that the HOMO levels are composed of binding π orbitals in oligothiophenes.[12] The origin of these π orbitals can be assigned to the thiophene rings. Interestingly, the interaction between the rings can be observed as the splitting of the bonding π orbitals where the number of the split levels corresponds to the number of interacting thiophene rings.[11] The same behavior can now be observed in the HOMO and HOMO-1 levels of BMB-2T and BMB-3T. The HOMO and HOMO-1 of BMB-2T probably
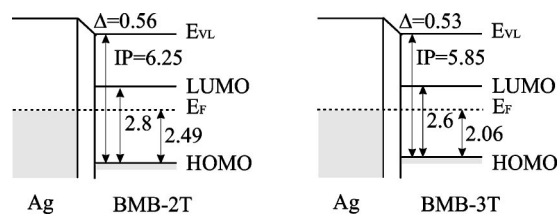
FIG. 3. The energy level alignment at the metal–organic interface. The energy values are expressed in eVs.

correspond to the π orbitals of the two thiophene rings, whereas the HOMO of BMB-3T is shifted to the lower binding energy, which is most likely a result of further level splitting in the three-member thiophene chain of BMB-3T. Conversely, following the treatments of oligothiophene spectra[12] we attribute the feature at 3.6 eV, which is independent of the number of thiophene rings, to the noninteracting orbitals in the repeating units. Additionally, our preliminary Hartree-Fock calculations[7] of the occupied energy levels of BMB-2T and BMB-3T are able to reproduce the experimentally observed HOMO shifts, and these calculations also indicate that the location of the HOMO is on the thiophene chain of each of the two molecules.

It is also of interest to consider the conjugation limit found in polythiophenes and in their derivatives. It has been found that as the conjugation length of the oligothiophene chain is increased beyond 7–8 thiophene rings,[12] the photoemission spectrum of the oligothiophene cannot be distinguished from that of the polythiophene.[11,14] In a polythiophene spectrum, the HOMO feature is a band-like distribution of levels originating from a large number of interacting thiophene rings.[11] The difference between the HOMO position of terthiophene and that of polythiophene is approximately 0.5 eV.[12] This gives an estimate for the upper limit of the HOMO of BMB-nT series molecules with a longer chain length.

The ionization potential (IP) of a molecular film is equal to the difference between the HeI photon energy and the width of the HeI spectrum. The latter is the difference of the intensity thresholds at the lowest and at the highest binding energies. Hence, the shifted HOMO levels of the two molecules imply different IPs, which were found to be 6.25 eV for BMB-2T and 5.85 eV for BMB-3T.

The energy level alignment at the metal–organic interface is shown in Fig. 3. The optical band gap was estimated from the absorption spectra of the solid films,[15] and was found to be 2.8 and 2.6 eV for BMB-2T and BMB-3T, respectively. Since the vacuum level shifts of BMB-2T and BMB-3T (Δ in Fig. 3) are practically the same, the difference in the ionization potentials is reflected in the positions of the molecular HOMO and lowest unoccupied molecular orbital

(LUMO) levels with respect to the Fermi level of the metal. Assuming the same exciton binding energy (typically 0.2 - 0.5 eV[16]) for both molecules, the estimated difference in the LUMO-Fermi level separation for the molecules is $\sim$0.2-0.3 eV. Here it is also useful to point out that in our analysis, we have used the flatband condition to determine the injection levels, i.e., the HOMO position indicated by flatband in Fig 3. is determined from the bulk film spectrum (64 Å), and the interface region of the energy levels (where level position is changing) is considered as a tunneling barrier for charge injection. Although, a real device would utilize a metal with a lower work function (the Ag foil used in the reported experiments had a work function of 4.32 eV), the estimated difference in barrier heights for BMB-2T and BMB-3T is indicative of what the energy level alignment at a metal–organic interface might be for the two molecules. Hence, electron injection into BMB-2T is expected to be more facile than that into BMB-3T due to the smaller barrier.

In conclusion, our UPS study of solid films of BMB-2T and BMB-3T has shown that the position of the HOMO level at the metal–organic interface is dependent on the number of thiophene rings of the molecules. We attribute the observed HOMO characteristics to the interacting π orbitals located on the thiophene rings. This will particularly affect the overall energy barrier for charge injection at the metal cathode, which will influence device performance. Therefore, these results need to be considered in the design of organic light-emitting diodes using these molecular structures.

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